REVIEW OF FIRE AND EXPLOSION HAZARDS
OF FLIGHT VEHICLE COMBUSTIBLES

TECHNICAL DOCUMENTARY REPORT NO. ASD-TR-61-278, SUPPLEMENT 1

October 1962

Flight Accessories Laboratory
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 6075, Task No. 607504

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FOREWORD

This report was prepared by the Explosives Research Laboratory of the U. S. Bureau of Mines, Pittsburgh, Pa. under USAF Delivery Order (33-616) 60-8. The contract was initiated under Project No. 6075, "Flight Vehicle Hazard Protection," Task No. 607504, "Fire and Explosion Characteristics of Aerospace Combustibles. The work was administered under the direction of Directorate of Aeromechanics, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. B. P. Botteri was the project engineer.

This report covers work done from April 1961 to April 1962 and is the second annual report on this contract.

ABSTRACT

The prevention of fires and explosions involving the combustibles
and oxidants likely to be found in flight vehicles requires a knowledge
of the flammability and related characteristics of these materials. This
report, the second in a series, presents the results of experimental
studies of certain phases of the general problem where information was
lacking or insufficient. These include: Ignition energy requirements and
limits of flammability of selected combustibles in oxidants other than air;
effect of blending of fuels on the spontaneous ignition temperature; effect
of temperature on the limits of flammability and minimum oxygen requirements
for flame propagation of selected combustibles; behavior of layered vapor
and liquid-vapor mixtures in various oxidizing atmospheres; behavior of
flame arrestors in static and in laminar and turbulent flowing mixtures.

This report has been reviewed and is approved.

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INTRODUCTION

This is the second annual report on the fire and explosion hazards associated with combustibles used in aircraft and missile systems. The first report (ref. 1) presented vapor pressure and flammability characteristics data for a number of combustibles and oxidants of interest. In addition, to assist in an understanding of these data the terms used in describing deflagration and detonation processes were reviewed briefly. The present report gives a summary of the data obtained here during the past year on additional combustible-oxidant systems of interest. In discussing these data, it has been assumed that the reader is familiar with the contents of reference 1.

RESULTS AND DISCUSSION

Although many studies have been conducted on the ignition, flammability and burning properties of the common organic solvents in air (ref. 2), little is known of their behavior in other oxidants which they may contact. Accordingly, ignition and flammability tests were conducted on four common solvents under a variety of conditions in air, oxygen, nitrogen tetroxide, and contaminated air atmospheres. In addition, ignition and flame propagation data were obtained for a number of miscellaneous hydrocarbon fuels in certain of these atmospheres.

Ignition

Electrical Sources

The concepts of minimum electrical ignition energy and quenching distance were discussed in reference 1. Measurements of these quantities are ordinarily made in air or in oxygen-nitrogen atmospheres. However, in the present study, the equipment developed at the Bureau of Mines (ref. 3) was used to determine minimum ignition energies and quenching distances for methyl alcohol, acetone, methylene chloride and trichloroethylene in air and in oxygen and, where possible, in nitrogen tetroxide atmospheres. The procedure used here was to first determine the most easily ignitible mixtures in each case and then to measure the minimum ignition energy and the quenching distance for glass-flanged electrodes in these mixtures. The results obtained with the four solvents and three oxidants are listed in Table 1. The minimum ignition energy data are also given in Figure 1 along with other data obtained here at atmospheric and reduced pressures. These latter data were used in obtaining the extrapolated values given in Table 1 for methylene chloride at one atmosphere; the experimental data were obtained at one-half atmosphere in this case.

In general, for the mixtures considered here, it would appear that the minimum ignition energy requirements are greatest for the solvent vapor-nitrogen tetroxide mixtures (when a hypergolic reaction does not occur) and least for the solvent vapor-oxygen mixtures. In the former case the results are affected quite markedly by the contact time between the vapor and oxidant; contact times of one to two minutes were used here to permit mixing. However, even these relatively short times may have affected the results obtained.

Hot Surfaces

A flammable mixture may be ignited by a hot surface if the temperature of the surface and the contact time are above the minimum values required for ignition at a specified pressure. The concepts of minimum autoignition temperature and contact time are of importance in establishing testing procedures for the evaluation of electrical, and electronic components.

Table 1. - <u>Minimum ignition energies and quenching distances for four solvents in air, oxygen and nitrogen tetroxide atmospheres.</u>

	Pressure (atm.)	Minimum Ignition Energy (millijoule)	Quenching Distance (mils)	Percent Combustible (vol.%)
<u>Air</u>				
Methyl alcohol	1	0.26	76**	12
Acetone	1	0.5	68**	5-7
Methylene chloride*	-	-	-	-
Trichloroethylene*	-	-	-	-
<u>Oxygen</u>				
Acetone	1	.0024	10**	15-30
Methylene chloride	1***	0.07	-	40
	1/2	0.28	65	45-65
Trichloroethylene	1/8	-	200**	60
<u>Nitrogen Tetroxide</u>				
Acetone	1/2	-	145	45
	1	-	72	45
Methylene chloride	1/2	2***	100***	60-70
	1	0.5	200	60-70
Trichloroethylene*	-	-	-	-

* Due to large electrode separation required, these tests were not
    feasible with the present equipment.
** Not necessarily the lowest quenching distances.
*** Extrapolated value.

For example, in determining the highest surface temperature that can be tolerated by a flammable mixture, both the mixture composition and surface temperature are varied. However, acceptance tests are ordinarily conducted on an electrical or electronic component that may come in contact with a flammable mixture at a single mixture composition. This mixture may be prepared by the method of partial pressures. When the fuel is a liquid blend, the composition of the vapor above the liquid is affected by the temperature and history of the liquid sample. Since the quantity of vapor required for a specified (e.g., stoichiometric) mixture depends on the composition of the vapor (e.g., the stoichiometric composition of butane in air is 3.12 volume percent, of pentane in air is 2.55 volume percent, of n-hexane is 2.16 volume percent, of n-decane is 1.33 volume percent, etc.) it is difficult to prepare the most easily ignitible fuel blend vapor-air mixture. For this reason, there is some merit in using single component fuels in preparing the mixtures to be used in components acceptance tests. Where a two-component fuel is chosen to give a mixture with a specified minimum autoignition temperature (A.I.T.), data should first be obtained for a variety of mixture compositions. Such data are given in Figure 2 for three blends and JP-6. In addition, the corresponding time delays or contact times for ignition are listed in parentheses near each experimental point. Thus we see that in place of JP-6, one could use pure hexane which has a slightly lower A.I.T. value or the appropriate pentane-hexane or pentane-heptane mixture. In each case the time lag for ignition is less than that obtained with JP-6; however, this would not be especially significant in most cases (Appendix I).

Flame Propagation

Homogeneous Systems

Limits of Flammability

Most experimental limits of flammability data have been obtained at ordinary temperatures and pressures (ref. 2). However, since the temperature and, to a lesser extent, the pressure affect the limits of flammability of a combustible-oxidant system, limits determinations should be conducted under the conditions likely to be encountered in practice. Accordingly, the lin 's of flammability of acetone, n-heptane, methyl alcohol, methylene chloride and trichloroethylene were determined at one or more elevated temperatures in air and in water vapor-air atmospheres. The data are summarized graphically in Figures 3 to 7. The third curve in Figure 3 was obtained at 617°F in the apparatus described in Appendix II using a 30-second mixing period. Using this curve and those obtained with other combustibles at elevated temperatures, the (solid) curves obtained at 212° and 392°F were corrected (broken curves) to yield the approximate prereaction mixture composition flammability curves at these temperatures.

The n-heptane-water vapor-air flammability curves were obtained in the Bureau of Mines elevated temperature apparatus at 212° and 392°F and

atmospheric pressure (Figure 4). The curve obtained at the lower tempera-
ture contained a single flammable mixture (hot flames) zone in which nor-
mal flames were obtained. A similar enlarged zone was obtained at 392°F;
in addition, a much larger zone was found above the upper limit curve in
which cool flames were observed (ref. 5). The cool flames were usually
quite pale but could be detected with a thermocouple placed near the upper
end of the flammability tube; such flames are important as they may lead
to ignition of mixtures in the hot flame mixture composition zone.

Limit-of-flammability tests were conducted on methyl alcohol-water
vapor-air mixtures at 212°, 392° and 752°F and atmospheric pressure in the
apparatus described in Appendix II. The minimum oxygen concentrations
appear to be too low when compared with the values obtained with the hydro-
carbons. However, since the methyl alcohol molecule (CH_3OH) contains a
large proportion of oxygen, these results are not surprising inasmuch as
this oxygen is involved in the combustion reactions.

Methylene chloride forms flammable mixtures in air and in a range of
water vapor-air mixtures at 392°F and atmospheric pressure (Figure 6).
The data presented here were obtained in a 4-inch ID tube; flame propaga-
tion was not obtained in this tube at room temperature so that even the
results obtained at 392°F may have been affected by the proximity of tube
walls. The presence of the walls may account for the rather large minimum
oxygen values found in this case (14.1 percent).

The data in Figure 7 illustrate quite conclusively that trichloro-
ethylene is flammable in air and in water vapor-air mixtures. As noted,
these data were obtained in a 4-inch ID tube. Preliminary experiments in
a 7-inch ID tube indicate that the flammable range may be even wider than
is indicated in Figure 7. In any event, this solvent must be treated as
a flammable material; additional work is required to determine the effect
of tube diameter on the flammable range.

Limit-of-flammability experiments were also conducted on the above
solvents in oxygen at various temperatures in a 2-inch ID stainless steel
tube (Appendix III). The data are presented graphically in Figure 8; as
usual, the flammable ranges were found to increase with increase in tem-
perature. An analysis of the lower limits data indicates that the effect
of temperature is given by the modified Burgess-Wheeler law (ref. 6) for
acetone, methyl alcohol and trichloroethylene. However, this law does not
predict the large decrease obtained with methylene chloride. Again, addi-
tional experiments must be conducted, especially at low temperatures and
with larger tubes to determine if the data for methylene chloride given
in Figure 8 were affected by the presence of the tube walls.

Flammability studies with nitrogen tetroxide as oxidant have shown
that this material is fairly reactive in contact with combustible vapors;
many materials ignite spontaneously on contact with it at ambient conditions.
Consequently, preliminary studies were conducted to determine the extent
of chemical reaction between the candidate materials and nitrogen tetroxide.

It was found that the reaction between a 35 volume percent acetone - 65 volume percent NO_2^* mixture (NO_2^* is the equilibrium mixture $N_2O_4 \rightleftharpoons 2NO_2$ at any specified temperature) was completed within about 5 minutes at 77°F and atmospheric pressure to form acetic acid, carbon dioxide and carbon monoxide. Under the same conditions, methyl alcohol and NO_2^* reacted in less than one second to produce formic acid; methylene chloride and tri-chloroethylene did not react appreciably. Autoignition tests showed that these materials do not ignite spontaneously in nitrogen tetroxide atmospheres below approximately 390°F. These results indicated that it was not feasible to determine the limits of flammability of methyl alcohol or acetone in nitrogen tetroxide with the standard equipment (ref. 2) since the rate of chemical reaction is considerably faster in each case than the mixing process. However, methylene chloride or trichloroethylene react slowly enough to permit limit-of-flammability determinations even at 212°F. Accordingly, limit-of-flammability tests were conducted on these materials in the apparatus described in Appendix IV. The results of these tests are given in Table 2. The lower limit values were found to be higher in nitrogen tetroxide than they were in oxygen. This is not surprising since the quantity of combustible required for complete combustion in nitrogen tetroxide is greater than that required for complete combustion in oxygen. The relatively large decrease obtained in the lower limit value of methylene chloride for a temperature increase of 135°F (from 77° to 212°F) is of interest. If the oxidant is assumed to be nitrogen dioxide or nitric oxide and oxygen at the higher temperature, the quantity of combustible required to complete combustion and the corresponding measured lower limit value would be decreased. On this basis it seems reasonable to assume that relatively large changes in the lower limits of flammability of materials in nitrogen tetroxide atmospheres are to be expected when the temperature is increased from room temperature where the nitrogen tetroxide exists primarily as N_2O_4 to some elevated temperature at which dissociation of the oxidant has occurred.

Table 2. - Limits of flammability of methylene chloride and trichloroethylene in nitrogen tetroxide at various temperatures.

	Lower limit of flammability (vol.%)			Upper limit of flammability (vol.%)	
	77°F	91°F	212°F	100°F	212°F
Methylene chloride	34.0	--	18.5	>78	--
Trichloroethylene	--	>12.7	16.3	--	67

An upper limit-of-flammability value could not be obtained for methylene chloride in nitrogen tetroxide at 100°F; a mixture containing 76 percent methylene chloride was still within the flammable range. At

212°F a vapor phase reaction apparently occurred since mixtures that originally contained 49 percent methylene chloride were not flammable.

Mixtures of trichloroethylene and nitrogen tetroxide with as much as 12.7 percent trichloroethylene were not flammable at 91°F. However, at 212°F the lower limit of flammability was found to be 16.3 percent. Because of the low vapor pressure of this solvent, an upper limit of flammability could not be determined at 100°F. Accordingly, a determination was made at 212°F.

Heterogeneous Systems

Combustible Vapor Layers in Air

Although heterogeneous gas mixtures are encountered more often in practice than homogeneous mixtures, considerably less is known concerning the flammability characteristics of the former; this is due primarily to the fact that the heterogeneous system is more complex. Since gases are subject to the laws of hydrodynamics, both laminar and turbulent burning are often involved in practice. The thickness of the turbulent layer preceding a flame front is dependent in part on the apparatus in which the flame is propagating and in part on the thermodynamic and transport properties of the gas mixture and the flame. For a specific apparatus and combustible-oxidant combination, one would expect to find a relatively constant turbulent layer thickness. In the burning of stratified layers of combustible-air mixtures in air, turbulence may influence the burning characteristics (pressure developed, burning velocity, etc.) of those systems in which large concentration gradients exist (e.g., 5 percent combustible/inch); little influence of turbulence would be expected in systems having low concentration gradients ($\sim$ 0.01 percent/inch). Therefore, the effects of turbulence on the burning properties of stratified combustible-air mixtures was investigated for the case of large concentration gradients.

Layers of various pentane-air mixtures in air were prepared and tested in the stratification apparatus described in Appendix V. Various interfacial concentration profiles were obtained for pentane-air mixtures by allowing the homogeneous combustible mixture (pentane-air) to diffuse upward for a predetermined time into a cylindrical container. The interfacial concentration profiles for each test condition were calculated from the gas diffusion equation for one-dimensional flow. The diffusion coefficient used in this calculation for pentane diffusing into air was determined from the theoretical expression of Curtiss and Hirschfelder (ref. 7). The results of these calculations for diffusional times of 0-, 1-, and 10-minutes are shown in Figure 9 where the dimensionless concentration ratio C_t/C_0 is plotted as a function of distance from the closed end of the cylinder; C_0 is the initial pentane concentration in the homogeneous combustible-air mixtures. Time is reckoned from the instant the homogeneous mixture is exposed to the surrounding air atmosphere. Typical pressure histories obtained in these experiments are given in Figure 10. In this figure, A shows a pressure record from a test in which the initial pentane concentration C_0 is above the upper limit of flammability (7.8 volume percent,

ref. 2) and a similar record, $\underline{B}$ for a mixture whose initial concentration is just below the upper limit. The pressure traces obtained in the former case show considerable fluctuations whereas those in the latter do not; the mixture compositions differed by about 1 percent in the two cases. These fluctuations were due to the turbulent mixing at the interface of the layers.

The maximum values of the pressures obtained in each of the above tests are plotted in Figure 11 as a function of the initial pentane concentration for diffusional times of 0 and 5 minutes. Also shown in the figure are the lower and upper limits of flammability (L.L. and U.L.) of pentane in air under ambient conditions. It is well known that in the combustion of most homogeneous gas mixtures, the maximum pressures increase from a finite but small value at the lower limit to a maximum value slightly on the fuel-rich side of the stoichiometric composition and then again decrease to a small value at the upper limit. However, we see from Figure 11 that for the heterogeneous mixtures the pressures developed during combustion depend, among other things, upon the interfacial concentration gradient as well as the initial fuel concentration. In the 0 min. ignition delay case (no diffusion), the maximum pressure rises monotonically to a maximum at fuel concentrations slightly leaner than the upper limit and then falls sharply to a relatively constant pressure on the fuel-rich side of the upper limit. The same situation holds true for the 5-minute ignition delay curve except that, in addition, since the interface has become more diffuse, a larger volume of gas mixture lies within the flammable zone prior to ignition. One would, therefore, expect to find higher combustion pressures over a wider concentration range with a less pronounced pressure drop at the interface. The results in Figure 11 support this expectation.

Flash-over Rates

Following the ignition of a liquid pool of combustible, a flame spreads quickly (flashes) over the liquid surface. The rate of spread (flash-over rate) of such a flame is an important burning characteristic. Consequently, the flash-over rates of acetone, methylene chloride, and trichloroethylene pools in air and in nitrogen tetroxide-air atmospheres were determined. The rate of flame spread was measured by photographic techniques. A high-speed framing camera operating at film speeds up to 1,000 frames per second was used to record the motion of the flame periphery following central ignition of a circular pool of liquid. The results found with acetone and methylene chloride are shown in Figure 12; the maximum rates are listed in the following table:

Combustible \ Atmosphere	Flame speeds (feet/second)		
	Air	NO$_2$*	50/50 Air-NO$_2$*
Acetone	36	No ignition	24
Methylene chloride	No ignition	12	No ignition

The curves in Figure 12 show that the flames initially accelerate away from the ignition source for a period of approximately 25 msec. before attaining a constant velocity. It is interesting to note that acetone does not support combustion in an atmosphere of pure NO_2^* and therefore has a lower flame spreading velocity in air containing NO_2^* than it does in air; the acetone and NO_2^* react on contact and probably generate a buffer zone of noncombustible products between the liquid surface and the NO_2^*-containing atmosphere. The results also show that although methylene chloride can not be ignited in air under ambient conditions, it can be ignited and burns in a nitrogen tetroxide atmosphere.

Pool Burning

As noted in reference 1, a combustible liquid burns by establishing a diffusion flame above the liquid surface. The gross rate at which the liquid level regresses is determined in part by the diameter of the liquid pool and has been found to follow the relation

$$v = v_\infty (1 - e^{-Kd}) \qquad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (1)$$

where K is the opacity coefficient, d the pool diameter, and v_∞ the liquid regression rate for large pool diameters, which can be expressed as

$$v_\infty = 0.003 \text{ x (net heat of combustion/sensible} \atop \text{heat of vaporization) inch/min.} \qquad - \quad - \quad (2)^*$$

for hydrocarbons burning in air. Figure 13 gives the liquid regression rates (burning rates) of a number of combustibles burned in relatively large trays in air (ref. 8). The burning rates of the pure fuels fall along the straight line given by the above relationship; the burning rate of the blended fuel (aviation gasoline) deviates from the predicted value by an appreciable amount.

Of primary concern in the present study was the applicability of equation 2 ro pure fuels burning in nitrogen tetroxide-air atmospheres. Accordingly, burning rate tests were conducted on acetone, methyl alcohol, methylene chloride and trichloroethylene in such atmospheres. Only acetone gave reliable results; methyl alcohol reacted very rapidly with the nitrogen tetroxide so that the data were rather erratic; methylene chloride and trichloroethylene did not support stable burning in this atmosphere at room temperature for a sufficient length of time to give reliable results.

Assuming the following stoichiometric reaction for acetone burning in nitrogen tetroxide,

$$(CH_3)_2 CO + 2N_2O_4 \longrightarrow 3CO_2 + 3H_2O + 2N_2$$
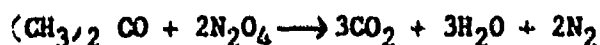
a consumption rate of 5.6 ft.^{3}/min. of nitrogen tetroxide vapor would be required for a liquid regression rate of 0.2 in./min. in a 10-inch diameter

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* The constant (0.003) was incorrectly given as 0.03 in reference 1.

tray. In practice, even larger flow rates would be required to assure an adequate supply of oxidant. Because of the toxicity of this oxidant, all burnings were conducted in trays with diameters of less than 6 inches. A description of the apparatus used in these experiments is given in Appendix VI. A summary of the data obtained in three trays is given in Figure 14. Substituting the liquid regression rate for acetone in a 5-inch diameter tray burning in air (see Figure 14) into equation 1 and assuming a value of 0.75 for K we obtain 0.18 in./min. for v_∞. Referring to Figure 13, this value (dashed line B) corresponds to a ratio $\Delta H_c/\Delta H_v$ of approximately 64. This is in satisfactory agreement with the corresponding value of 60 obtained from the heats of combustion and vaporization of acetone. If a similar calculation is made for the burning of acetone in an NO_2^*-air atmosphere using the data of Figure 14, a value of 0.30 in./min. is obtained for v_∞. This value (dashed line A in Figure 13) corresponds to a $\Delta H_c/\Delta H_v$ ratio of 110. However, the maximum value of $\Delta H_c/\Delta H_v$ that can be envisioned for this combustion process is 80, corresponding to the following reaction:

$$(CH_3)_2CO + 8NO \longrightarrow 3CO_2 + 3H_2O + 4N_2$$
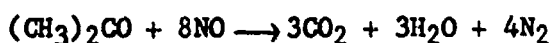
The NO required in this reaction would presumably be formed by the thermal decomposition of NO_2^*. A value of 80 would therefore be too high since the thermal energy expended in the decomposition of NO_2^* was neglected; furthermore, some of the acetone would be consumed by the oxygen in the NO_2^*-air mixture, thereby lowering the net heat of combustion still further. On the basis of these results it seems reasonable to conclude that liquid pool burning in NO_2^* atmospheres does not follow the semi-empirical relationship shown in equation 2. Apparently a new value must be obtained for the co-efficient (0.003) of the heat ratio to account for the increase in burning rate obtained in the nitrogen tetroxide-air atmosphere.

Flame Arresters and Flash Back of Flame

Flame arresters have been used for a number of years to prevent the passage of flame into an inhabited or other critical area. However, very little work was conducted on the properties of such arresters in other than quiescent atmospheres. The recent work of Palmer on wire gauzes (ref. 9) and on perforated sheets and blocks (ref. 10) was an attempt to relate performance of arresters to the properties of the flames, the nature of the flammable mixture and the dimensions of the system in which the arrester was installed. A summary of the data obtained by Palmer with brass and phosphor-bronze arresters at atmospheric pressure and 63°F is given in Figure 15 (curves 1, 2 and 3); flames were initiated at the base of an open 2.5-inch tube containing various propane-air-oxygen and ethylene-air-oxygen mixtures. Curves 1 and 2 were obtained with propane and curve 3 with ethylene. To use the data given in Figure 15, note that an arrester prevents the passage of flame if the flame approach velocity lies in the area below the performance curve for a particular combustible but does not prevent its passage if the flame approach velocity lies in the area above the curve.

Thus, a wire gauze with an 0.01-inch opening can stop flames from propagation upward through a propane-air-oxygen mixture at 63°F and atmospheric pressure in a 2.5-inch tube if the approach velocity of the flame is less than about 58 ft./sec. and the flame run-up distance is 44 inches. The run-up distance appears to affect the performance of an arrester slightly (compare curves 1 and 2); this may be due to the effect of the run-up distance on the flame shape.

Curves 4 and 5 (Figure 15) were also obtained with wire gauze arresters. Curve 4 was constructed from Holm's data on methane and natural gas (ref. 11); curve 5 was constructed from the data obtained with pentane-air mixtures during the present investigation (Appendix VII). Curves 1 through 5 define a performance band for commercial wire gauze arresters. To improve this performance, one must use tube bundles or perforated blocks (ref. 10). In the present study, the efficacy of three tube bundles was determined in stationary and moving pentane-air mixtures. The data are given as summary points 6 and 7 and an approximate curve between points 8 and 9 in Figure 15. Points 6 and 7 were obtained with a bundle of 0.25-inch OD by 0.181-inch ID by 6-inch tubes tightly packed in a 2-inch glass pipe. The tubes were made of 304 stainless steel and were held in place with two 4-mesh galvanized iron screens (0.22-inch opening formed by 0.024-inch wire). The pentane-air mixtures were stationary or moved very slowly in each case. Flame propagation was upward in the experiments used to define point 6 and downward in the experiments used to define point 7. Further, the rapid speeds attained by the upward propagating flames in case 6 produced turbulence in the 2-inch flame tube; the flames were laminar in case 7. Performance point 7 was also obtained with an aluminum tube bundle similar to the stainless steel bundle.

Performance point 6 appeared to shift upward when the flammable mixture moved through the tube bundle at a high speed before ignition. That is, the tube bundle was apparently more efficient in a high-speed stream than in a quiescent atmosphere. A tube bundle made of 0.0937-inch OD by 0.0857-inch ID by 6-inch stainless steel tubes packed in a 2-inch glass pipe did not permit flame propagation in either stationary or high-speed streams (point 9); the flame velocity approached the speed of sound in the latter experiments.

All flame arrester experiments were conducted at atmospheric pressure and room temperature. Since a decrease in pressure or temperature would tend to increase the arrester opening required for flame propagation, the performance band given in Figure 15 would probably be shifted upward so that an arrester that is adequate for use at atmospheric pressure would also be adequate for use at reduced pressures.

When a flammable vapor-air mixture is ignited at the outlet of a tube through which it flows, the resultant flame may blow off, may attach to the tube or flash into the tube toward the arrester. Flames propagate back through stoichiometric pentane-air mixtures flowing out of a 2-inch tube at velocities up to about 150 ft./sec. When an air stream flows around the 2-inch tube in the same direction as the flammable mixture, a flame can be

stabilized at the outlet at velocities between 10 and 110 ft./sec. At about 8 ft./sec., the flame flashes back into the 2-inch tube, so that an arrester would be needed to prevent propagation of flame upstream at these speeds. Experiments were not conducted in slow streams flowing out of a tube into fast air streams so that performance of flames under these conditions cannot be assessed at present.

SUMMARY AND CONCLUSIONS

Electric spark ignition experiments conducted to date on various combustibles in oxygen, air and nitrogen tetroxide atmospheres indicate that for a particular combustible, when autoignition does not occur, the energy requirements for ignition are greater in nitrogen tetroxide atmospheres than they are in air or oxygen. Further, the quenching distance is larger in a flammable vapor-nitrogen tetroxide mixture than it is in the corresponding mixture (e.g., a stoichiometric mixture) in air.

Flammable vapor-air mixtures can be prepared with simple, preferably single component, fuels to replace the flammable mixtures prepared from fuel blends for use in electrical and electronic components acceptance tests. Of primary importance is the selection of a simple fuel to yield mixtures with a minimum autoignition temperature and an electrical ignition energy requirement equal to that of the more complex fuel blend.

An increase in ambient temperature tends to widen the flammable range of a combustible in air, oxygen and nitrogen tetroxide atmospheres. At elevated temperature, this effect may be marked by the presence of oxidation reactions that proceed during the time required to prepare a test mixture.

The amount of water vapor required for flame suppression increases as the initial flammable mixture temperature increases; conversely, the oxygen requirements for flame propagation decreases with increase in temperature.

Layers of nonflammable vapor-air mixtures in air can be burned if a flammable vapor-air interface is ignited. The burning process is not as smooth as it is with flammable premixed mixtures since burning is preceded by the mixing of the nonflammable mixture with air, following ignition.

Pool burning of certain flammable liquids can occur in nitrogen tetroxide, and nitrogen tetroxide-air mixtures. Where the liquid reacts to any great extent on contact with the nitrogen tetroxide, an inert buffer zone may be produced which makes vapor ignition quite difficult.

The performance of a flame arrester in a flowing stream appears to be governed in part by the nature of the flammable stream, the dimensions of the arrester, the flame speed, direction of flame propagation, and scale of turbulence of the mixture flowing into the arrester.

Flames propagate upstream more readily through a flammable mixture flowing into quiescent air than they do through a flammable mixture flowing into air that moves at the same velocity.

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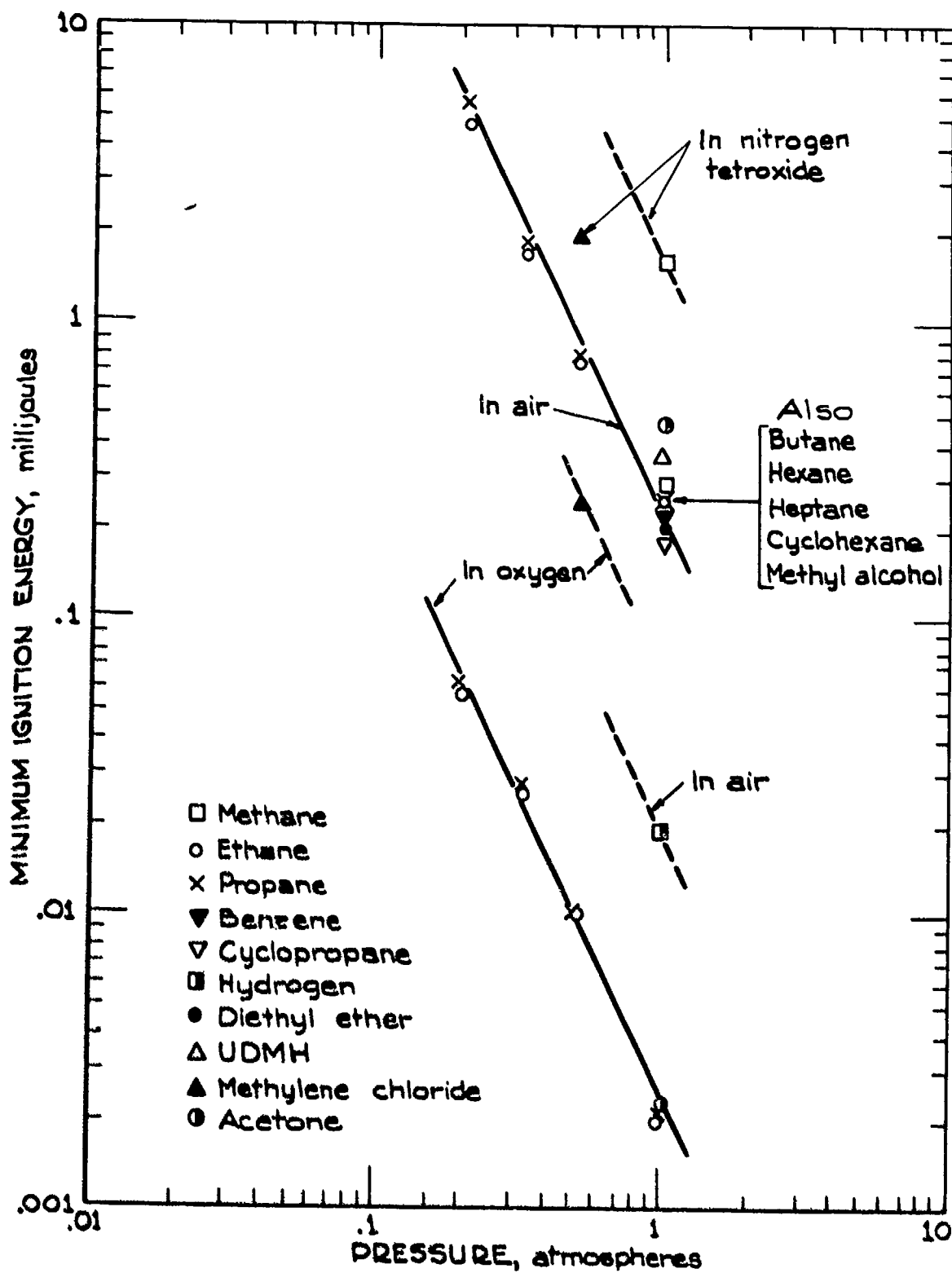
Figure 1. - Minimum ignition energies of certain gases and vapors in various atmospheres.
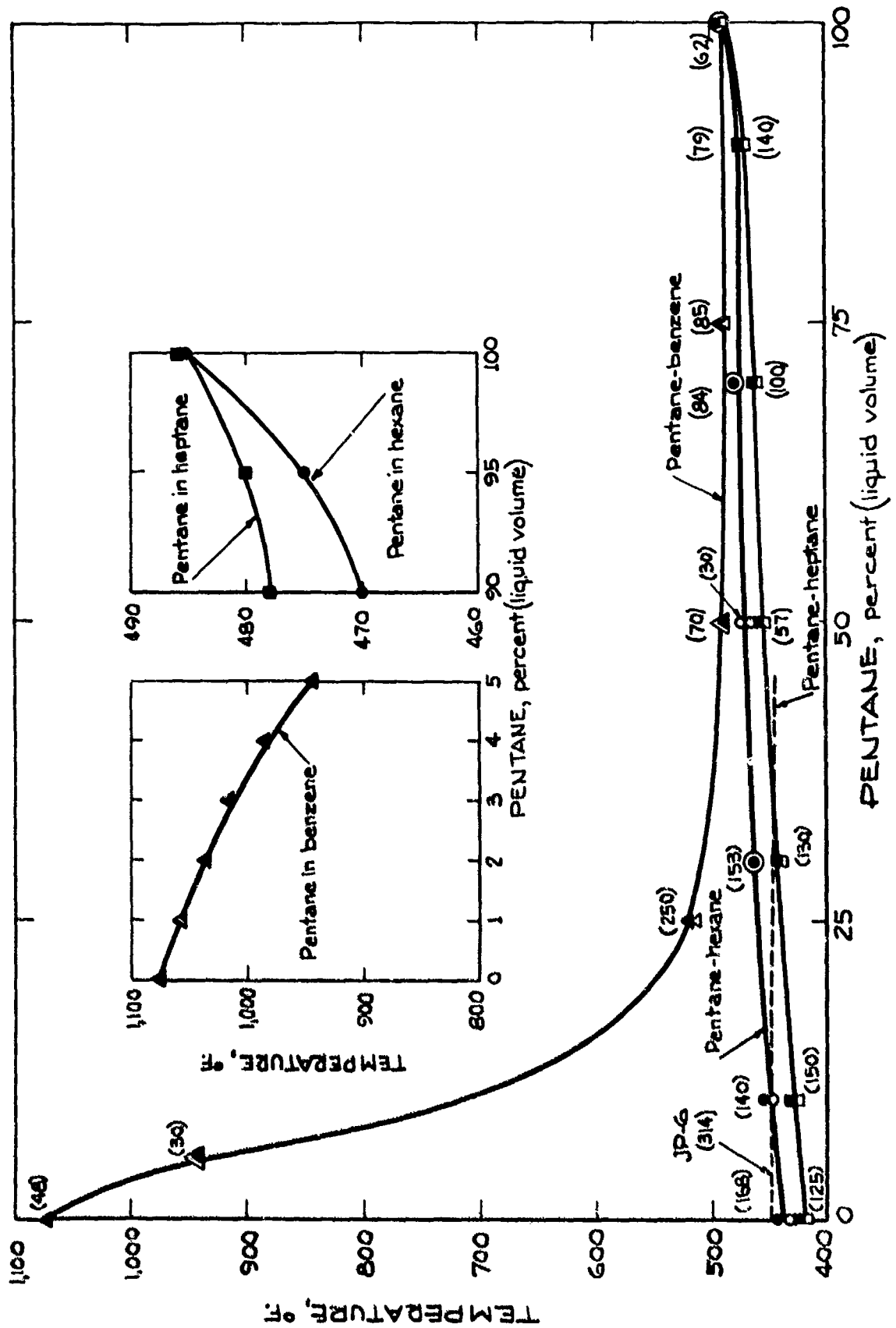
Figure 2. — Autoignition temperatures of fuel mixtures in a 173 cu.in. bomb at atmospheric pressure. (Figures in parenthesis are lag time in seconds).
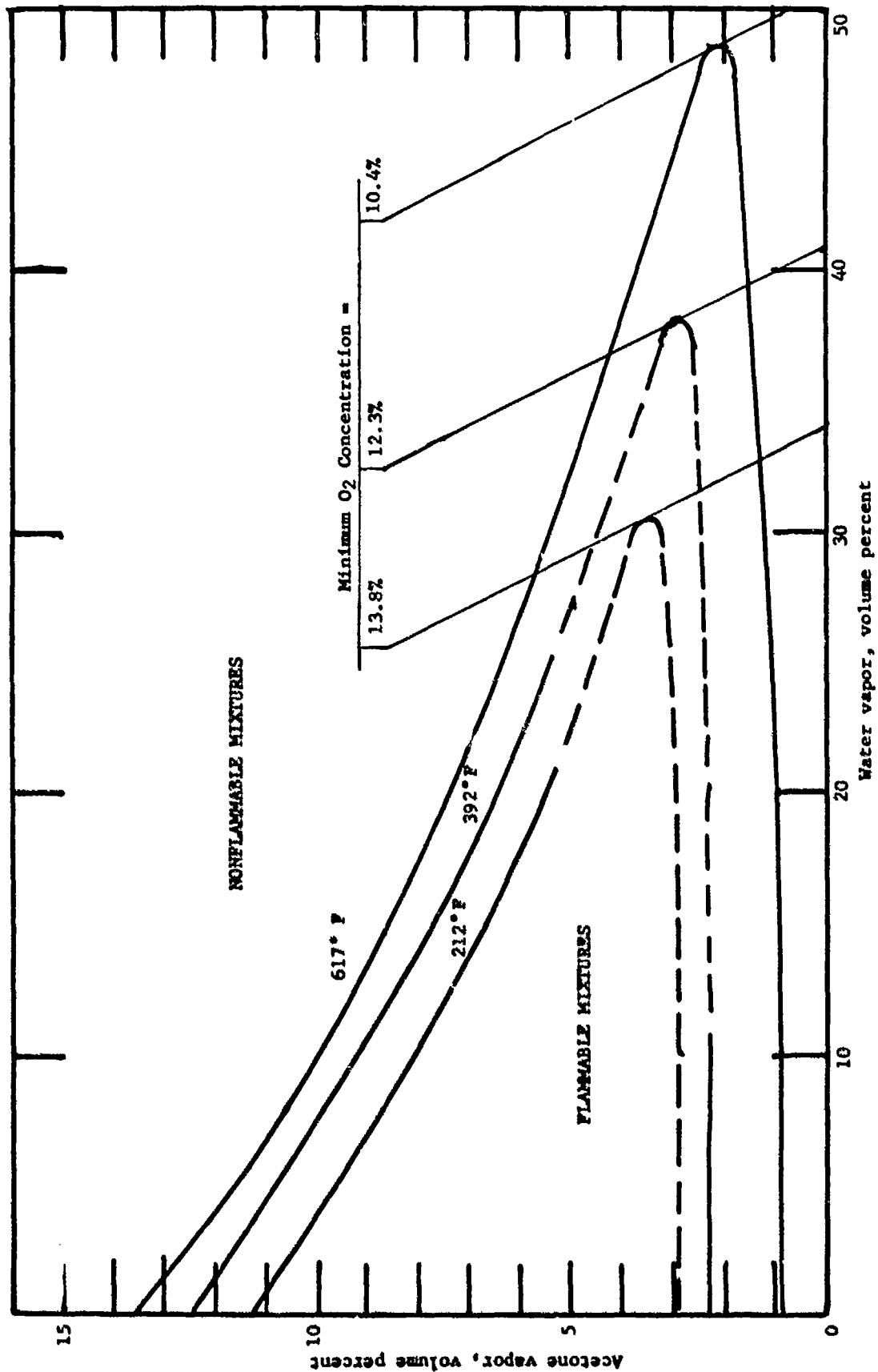
Figure 3. - Flammability of acetone-water vapor-air mixtures at 212°F., 392°F., and 617°F. and atmospheric pressure.
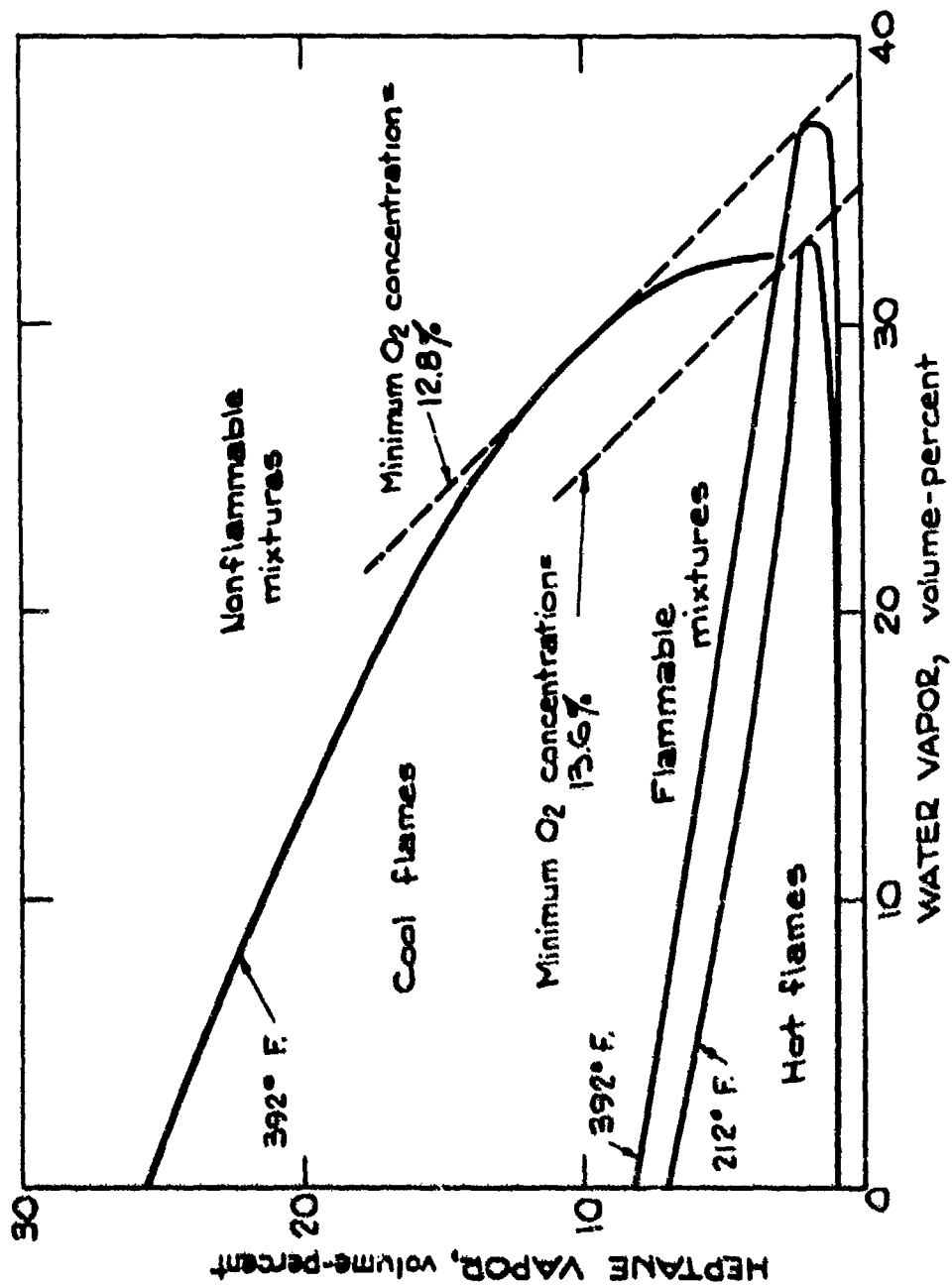
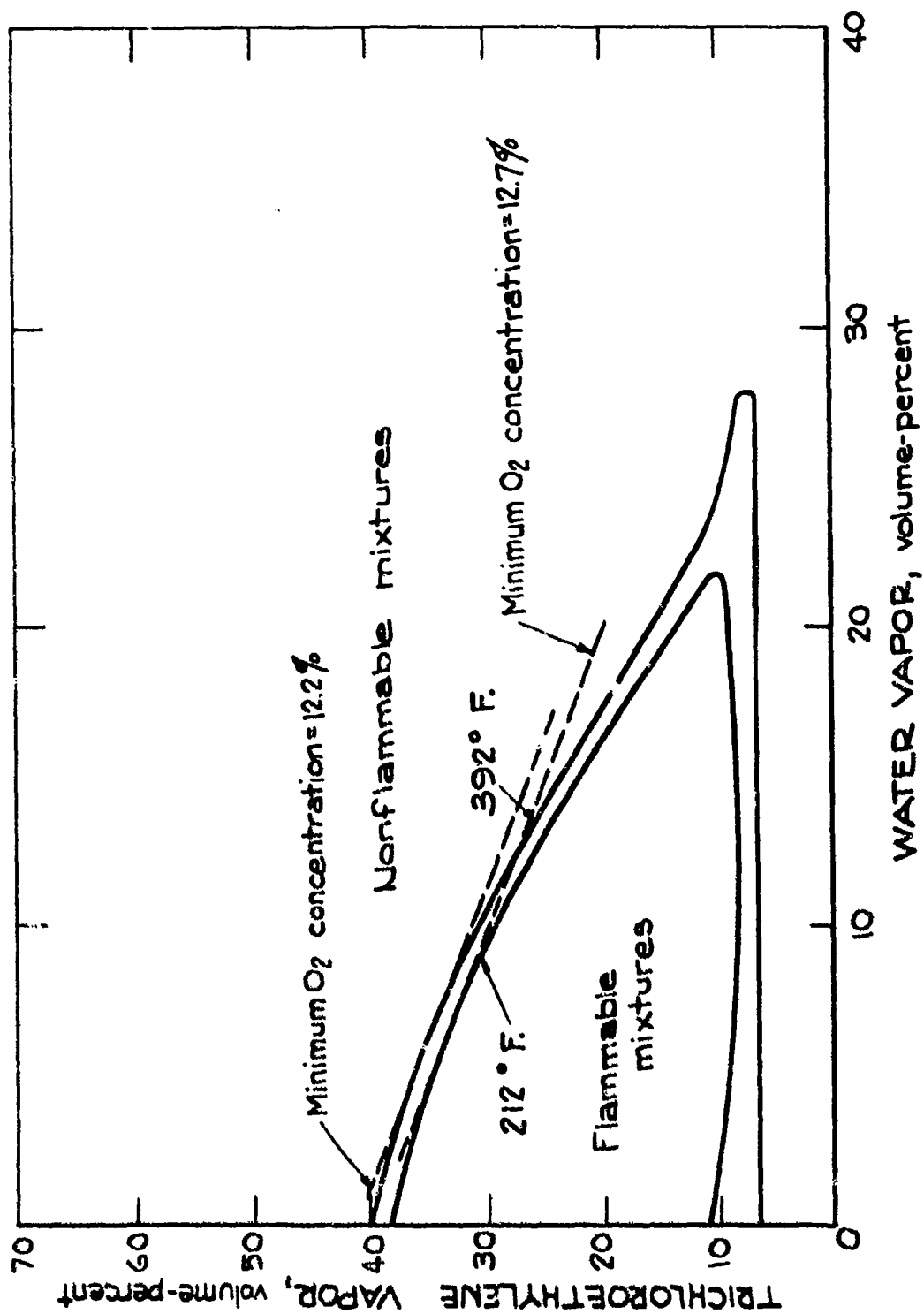Figure 4. - Flammability of n-heptane-water-air mixtures at 212° and 392°F. and atmospheric pressure. Cool flames at 392°F. are also shown.
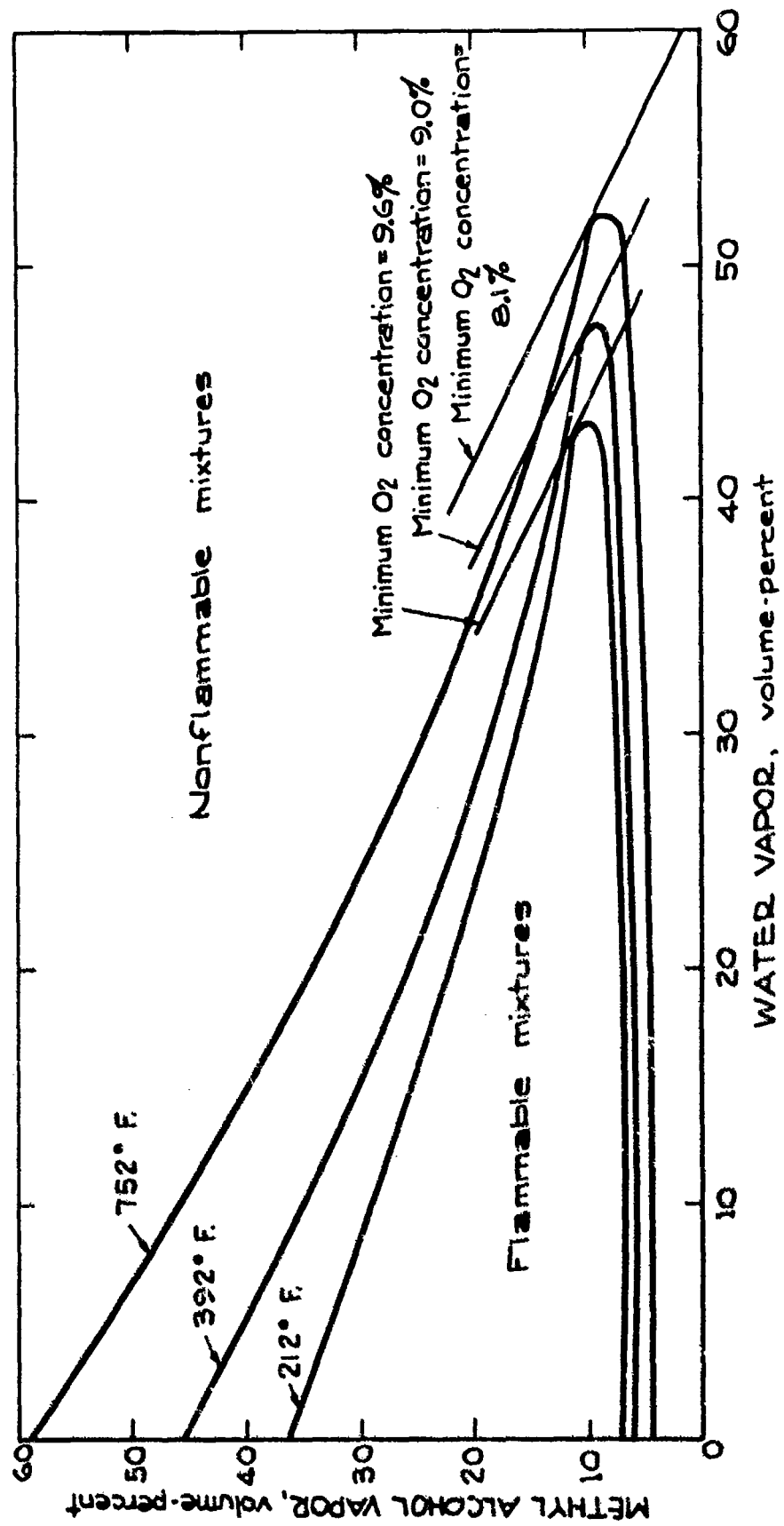
Figure 5. - Flammability of methyl alcohol-water-air mixtures at 212°, 392°, and 752°F, and atmospheric pressure.
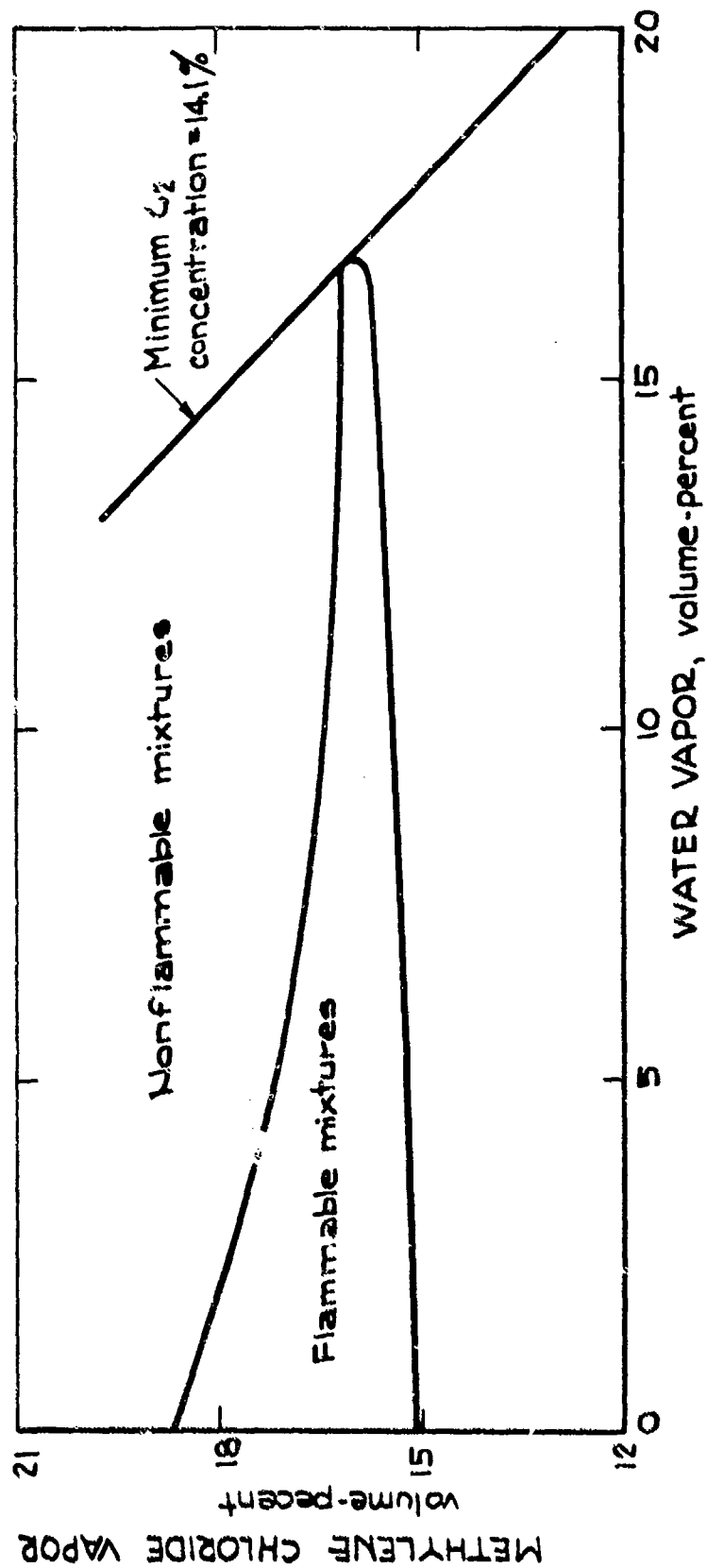
Figure 6. - Flammability of methylene chloride-water-air mixtures at 392°F. and atmospheric pressure.

Figure 7. - Flammability of Trichloroethylene-water-air mixtures at 212° and 392°F. and atmospheric pressure (F-11 apparatus, 4" ID tube).
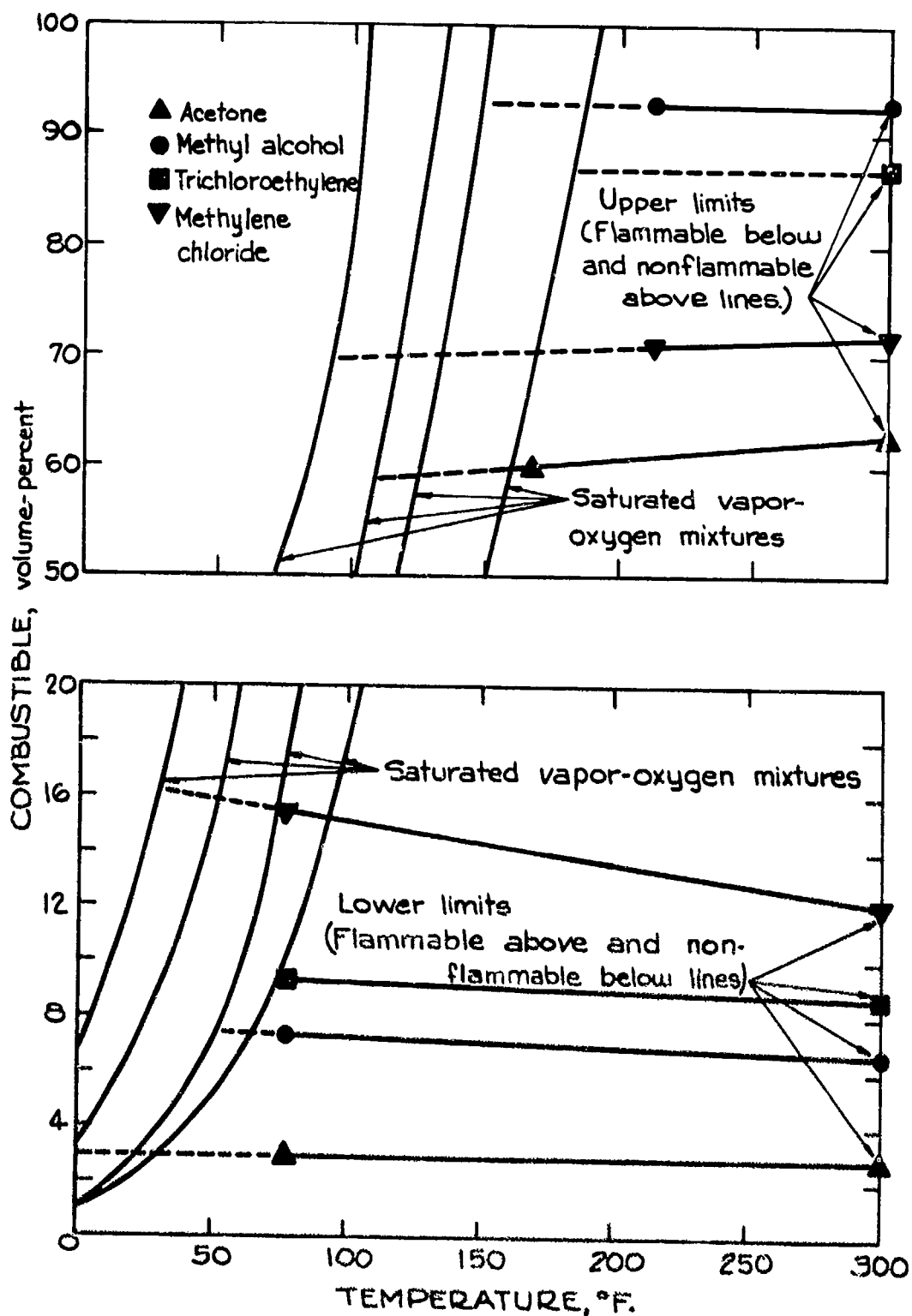
Figure 8. - Effect of temperature on limits of flammability of various combustibles in oxygen at atmospheric pressure.
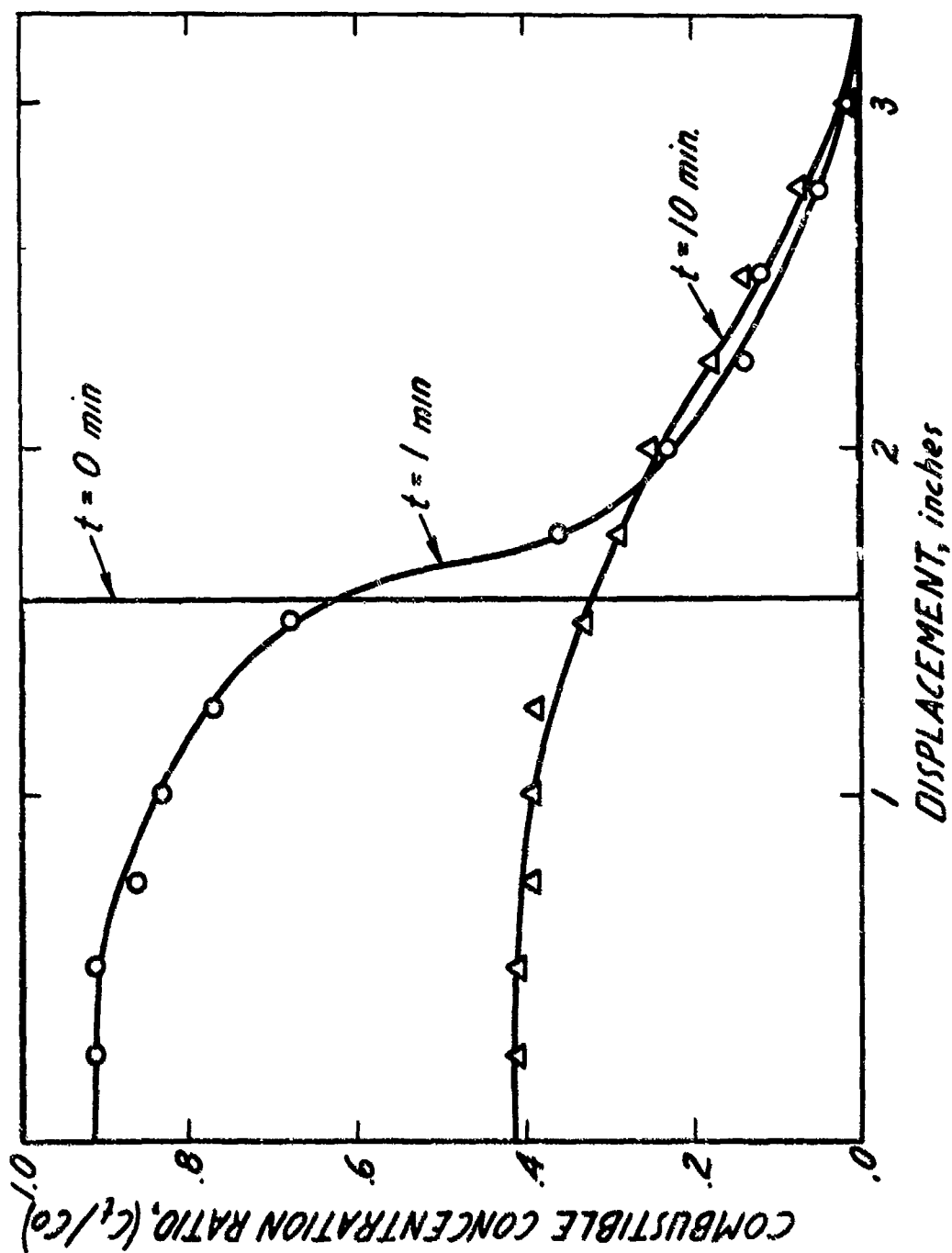
Figure 9. - Concentration profile of pentane diffusing into air following exposure of a homogeneous pentane-air mixture of initial concentration C_o.
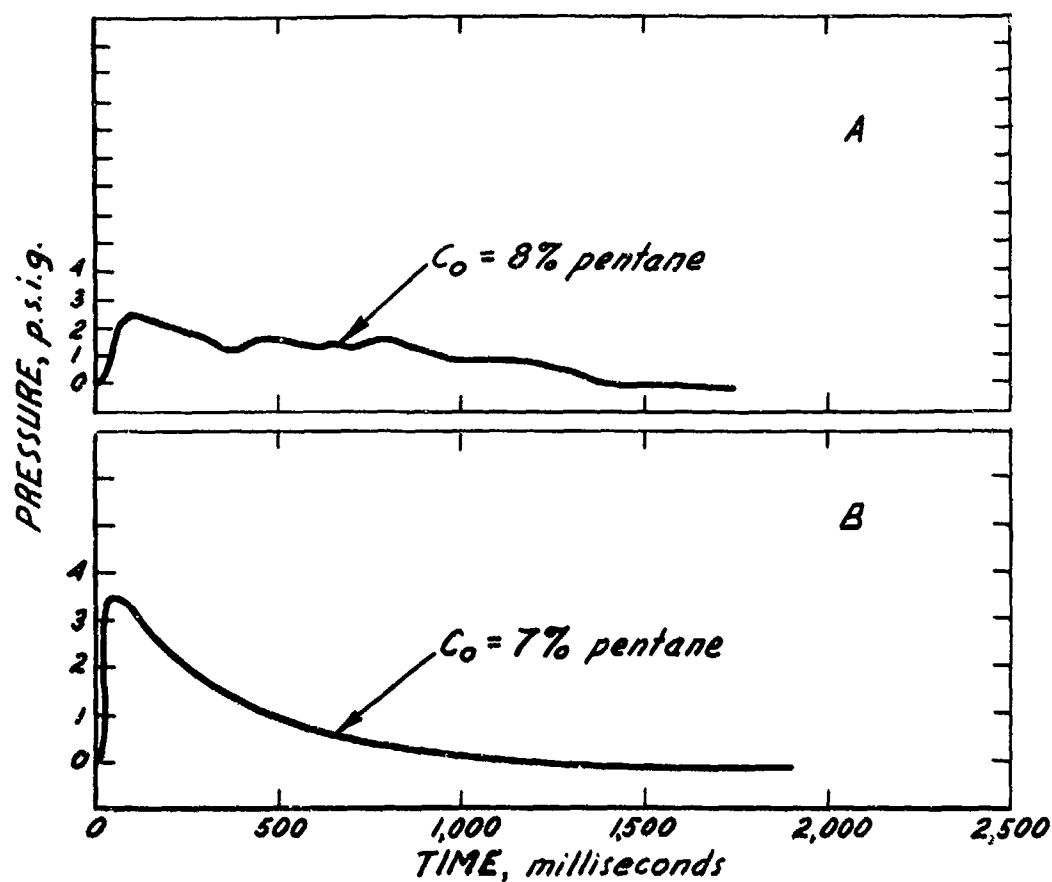
Figure 10. - Pressure histories following ignition of layered pentane-air mixtures in air for two initial pentane concentrations.
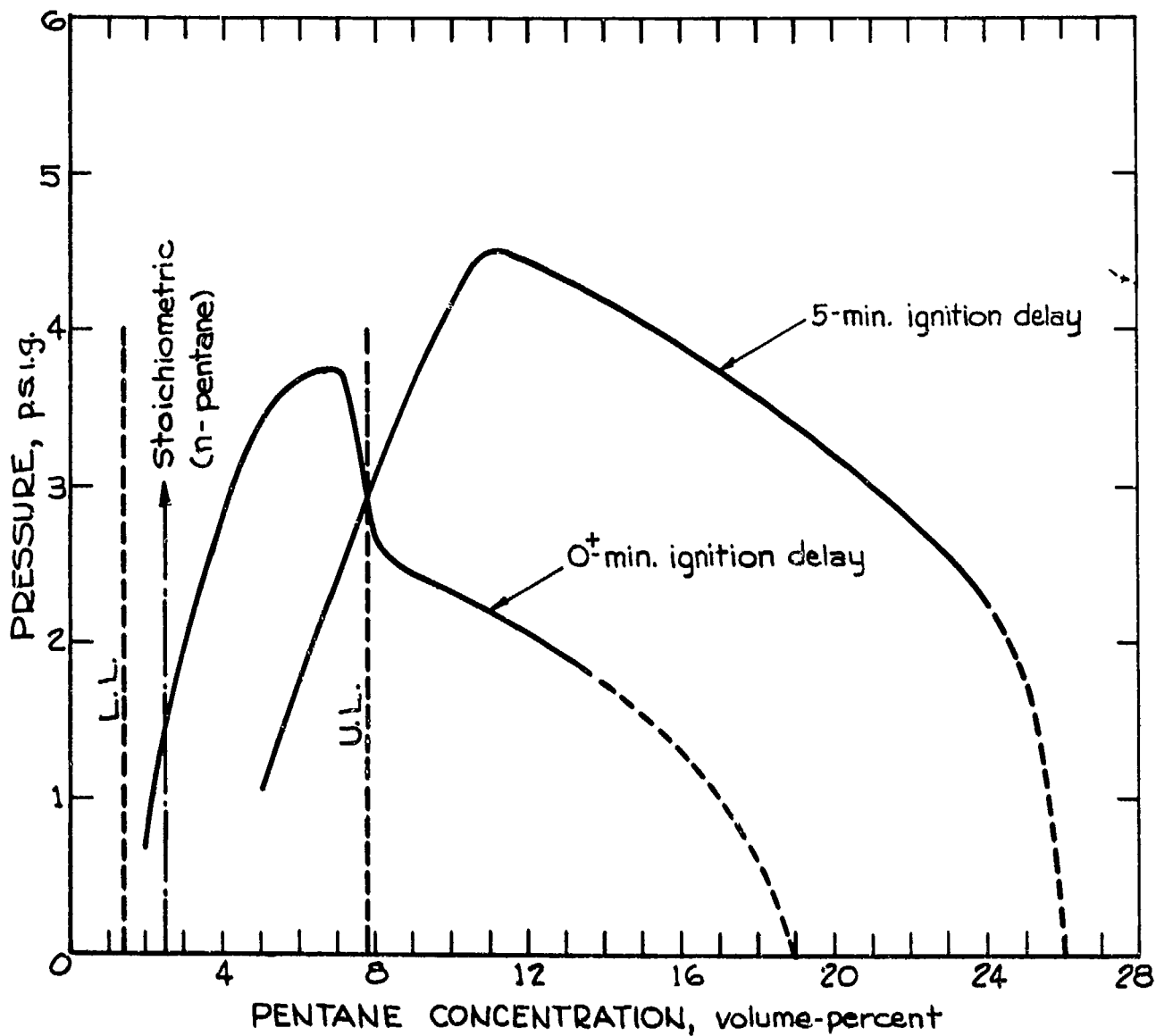
Figure 11. - Pressure developed during combustion of a stratified
mixture of pentane-air and air as a function of the
initial pentane concentration.
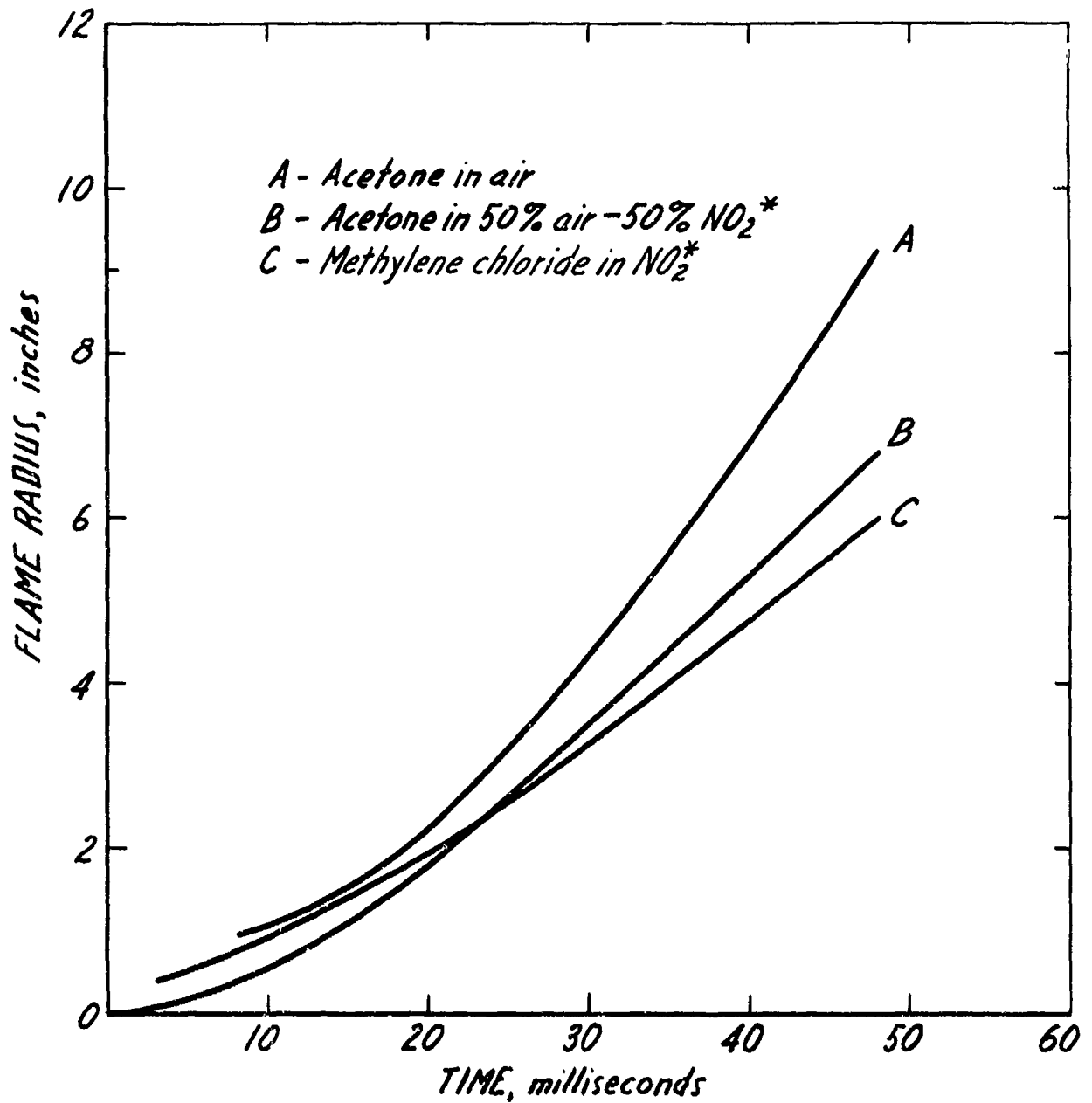
Figure 12. - Radius of flame periphery in a liquid pool surface as a function of time following ignition for three combustible-oxidant combinations.
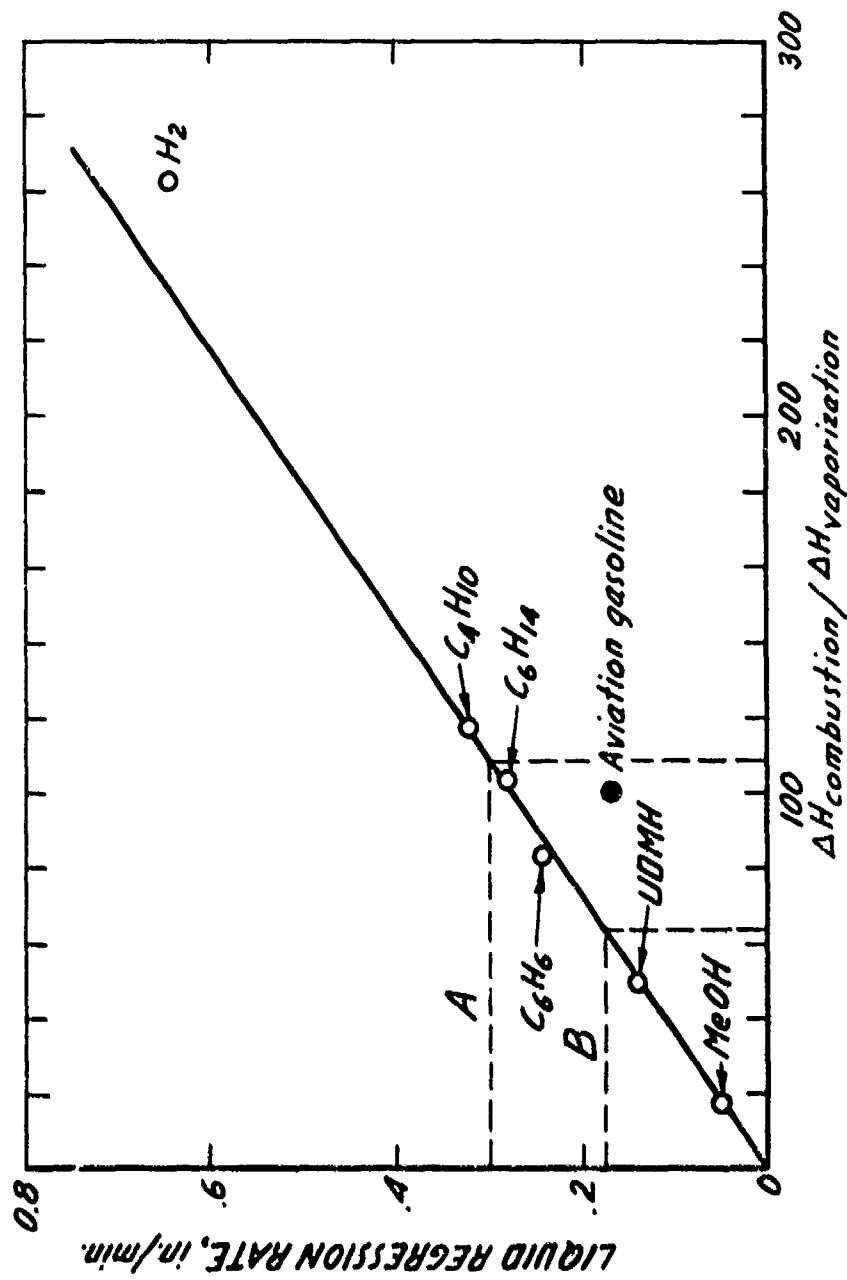
Figure 13. - Relationship of liquid regression rate at large tray diameter to two physical properties of fuel.
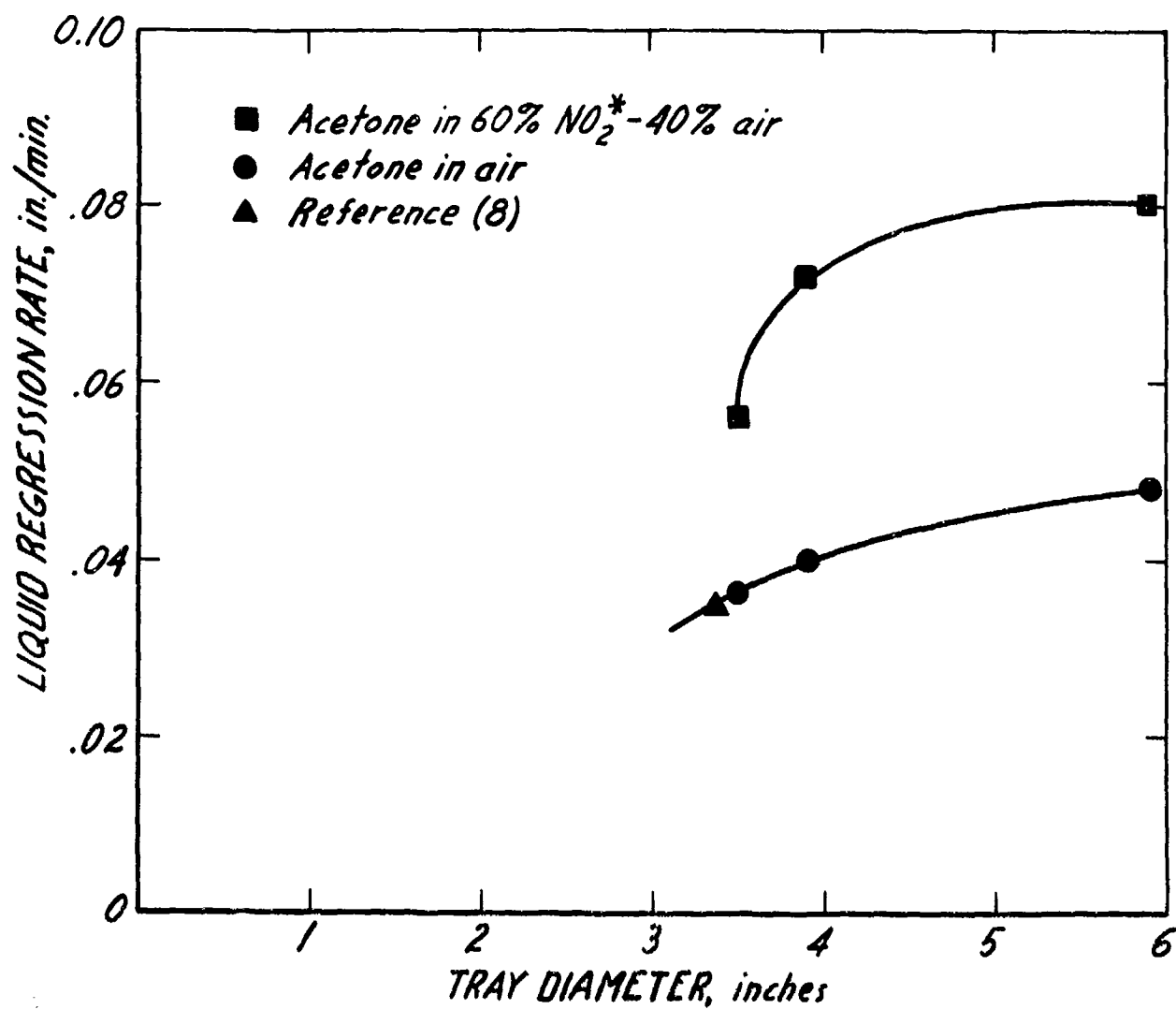
Figure 14. - Liquid regression rates of a burning pool of acetone in atmospheres of air and 60% NO$_2$*-40% air.
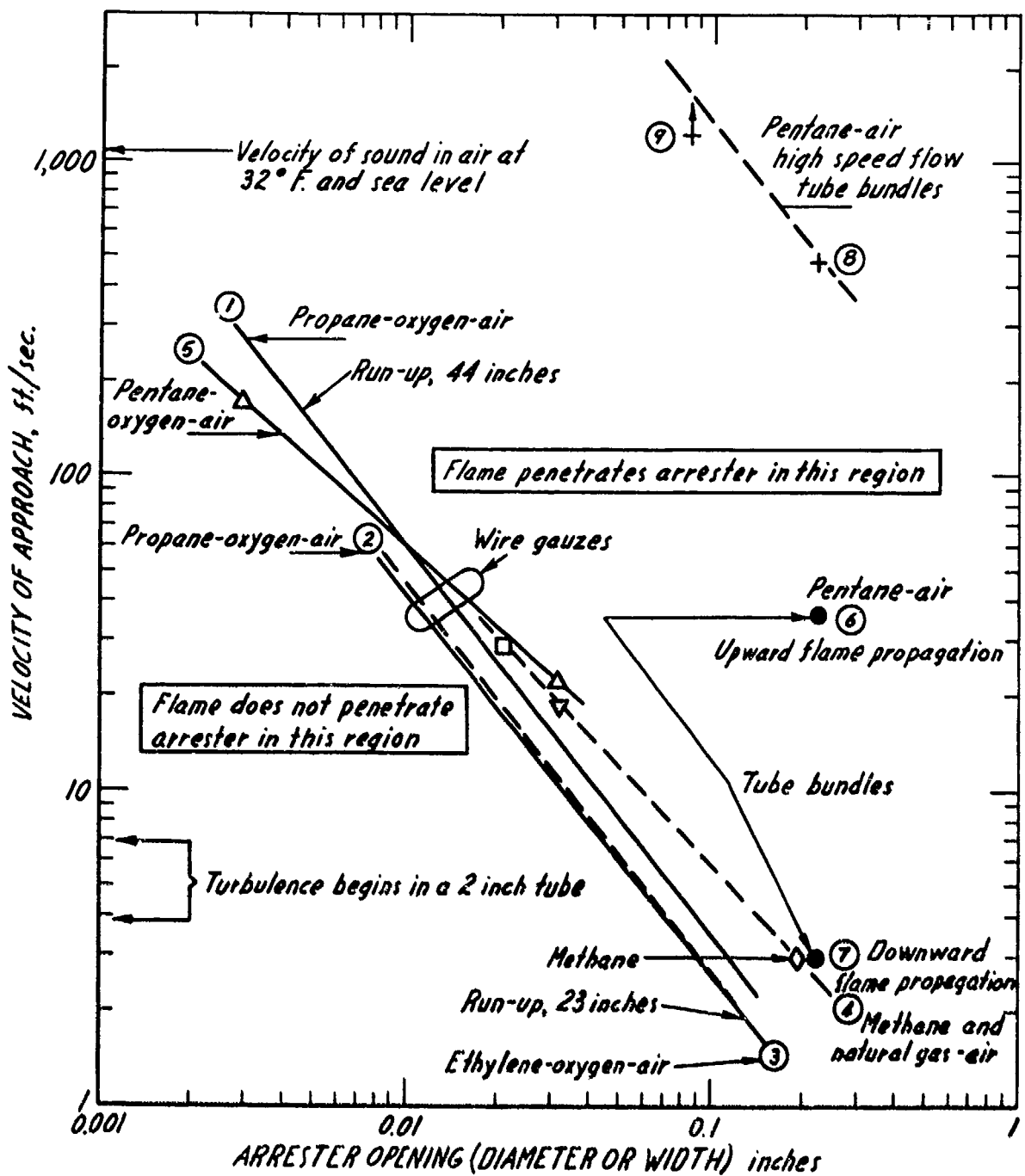
Figure 15. - Performance of various flame arresters in flammable atmospheres.

APPENDIX I

Autoignition Temperatures

The apparatus used to determine the autoignition temperatures of hydrocarbon-air mixtures is shown in Figure 16. To conduct a test, the test vessel (bomb) is first heated to the desired temperature. After 10 minutes it is evacuated and valves A and B are closed. The compressed air line is then disconnected and a measured sample of liquid fuel injected into the tubing above valve A; this valve is then opened to permit the fuel and air to enter the bomb rapidly. As soon as the bomb pressure is one atmosphere, valve A is closed and an electric timer started. The timer is stopped when the pressure within the bomb increases suddenly (a sudden pressure rise is used as the ignition criterion). If a pressure rise does not occur within six minutes, the temperature is considered to be too low for autoignition to occur. In either case, the plug valve is opened, the compressed air line reconnected, and the bomb cleaned with a stream of air. When ignition occurs, the bomb temperature is decreased and the test repeated; when ignition does not occur, the bomb temperature is increased and the test repeated, etc., until the lowest temperature at which ignition occurs is found. The sample volume is changed and the entire procedure is again repeated, etc., until the lowest temperature at which ignition occurs is found. The sample volume is changed and the entire procedure is again repeated, etc., until the minimum autoignition temperature (A.I.T.) is obtained.
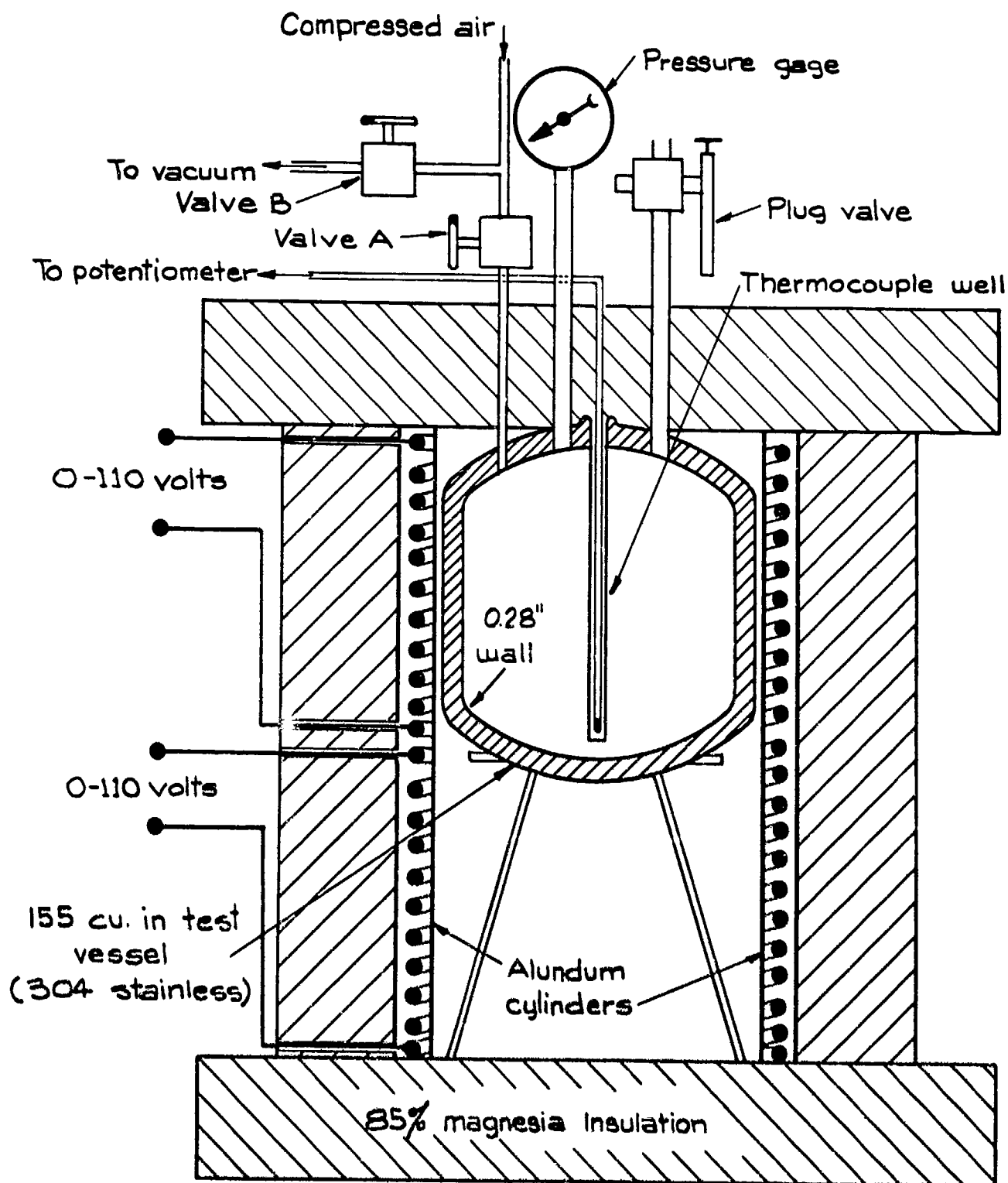
Figure 16. - Apparatus for determining autoignition temperatures
of hydrocarbon mixtures.

APPENDIX II

Limits of Flammability at Elevated Temperatures

Where possible, limit-of-flammability tests were conducted in the Bureau of Mines F-11 apparatus.[1,2] At temperatures above about 400°F limit determinations were made in an apparatus similar to that described in Appendix I. However, the bomb used in the flammability work was larger. (298 cu.in. instead of 155 cu.in. capacity) and also was equipped with an ignitor.

To conduct a test, the bomb was first heated to the desired temperature, evacuated and then isolated with valves A and B. A measured sample of liquid combustible was then placed in the tube above valve A. The sample was forced through valve A with water and air until atmospheric pressure was attained. Valve A was then closed, 30 seconds allowed for mixing, and then a short length of 36-gage platinum wire fused inside the bomb. A sudden deflection on a Bourdon-type gage was considered as evidence for flame propagation through a flammable mixture. If a pressure rise did not occur, the mixture was considered nonflammable.

1/ Zabetakis, M. G., Scott, G. S., and Jones, G. W. The Flammability Characteristics of the C_nH_{2n-6} Aromatic Series: Bureau of Mines Rept. of Investigations 4824 (1951), 9 pp.

2/ Zabetakis, M. G., Scott, G. S., and Jones, G. W. Limits of Flammability of the Paraffin Hydrocarbons in Air: Ind. Eng. Chem., Vol. 43, pp. 2120-2124 (1951).

APPENDIX III

Limits of Flammability in Oxygen

The apparatus used to determine the limits of flammability of methyl alcohol and acetone in oxygen at ambient temperature and atmospheric pressure is shown in Figure 17. It consisted of a stainless steel tube A, 2-inch ID and 43 inches in length, closed at each end and equipped with the necessary accessories to obtain a desired gas mixture by the method of partial pressures. Tube A contained a small teflon ball which served to mix the gases by falling through the tube which was slowly rocked about the horizontal position. Ignition was effected by the fusion of a short coil at 0.005-inch diameter platinum wire.

To conduct a test tube A was first evacuated, fuel vapor was then added from reservoir B until a predetermined pressure was obtained on manometer C. The system was brought to one atmosphere pressure with oxygen and the gases were mixed for one-half hour. The mixture was tested for flammability by fusion of the platinum wire at the base of the tube. A mixture was considered to be flammable if a pressure rise was obtained on gauge D following ignition.

Flammability tests were conducted at elevated temperatures by placing tube A inside an electrically heated oven. In this case, the desired gas mixtures were obtained by injecting weighed quantities of fuel into the evacuated system and adding oxygen until a pressure of one atmosphere was obtained.
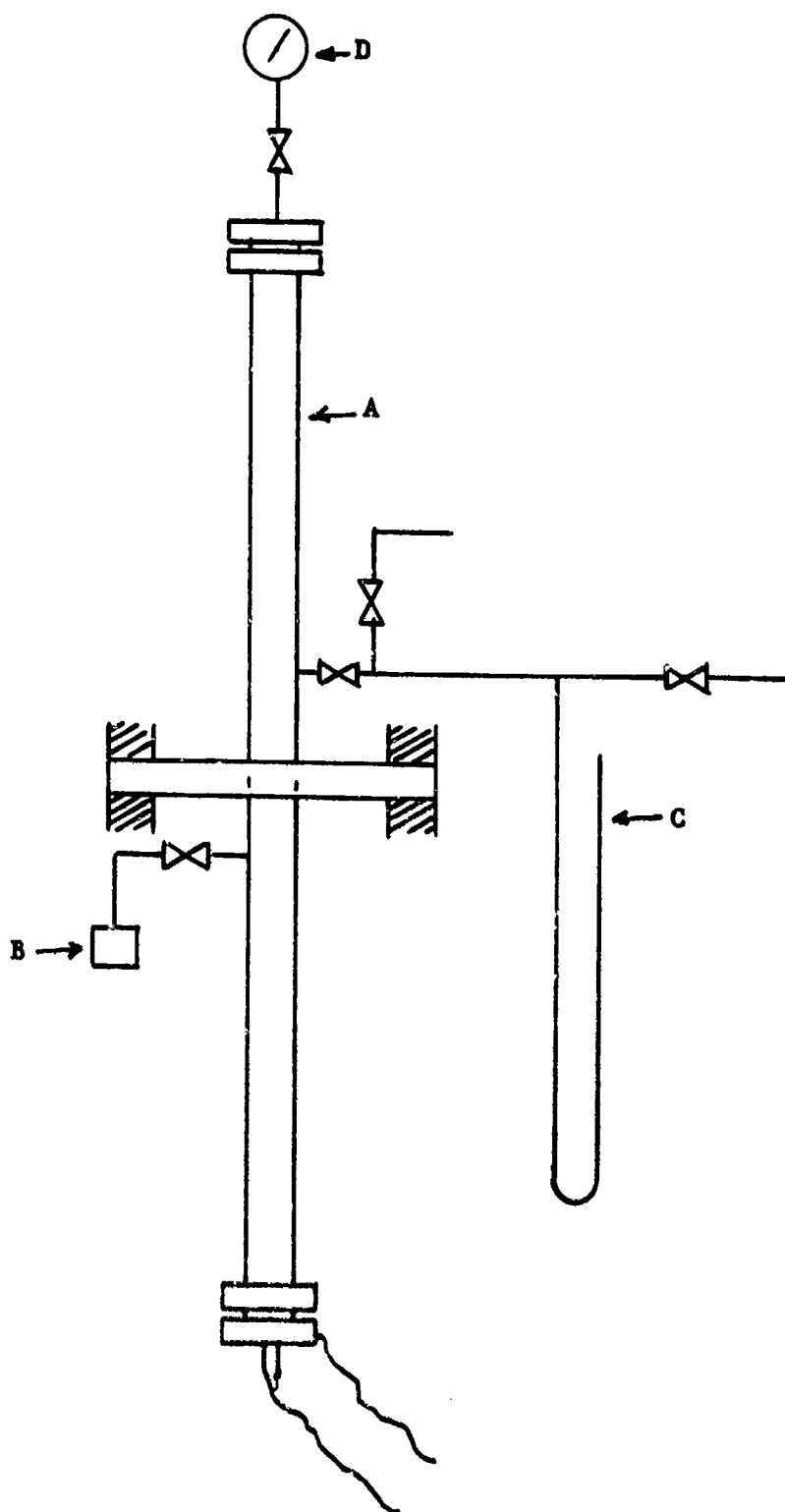
Figure 17. - Apparatus for the determination of limits of flammability in oxygen at ambient temperatures and atmospheric pressure.

APPENDIX IV

Limits of Flammability of Mixtures
Containing Nitrogen Tetroxide

Limit-of-flammability determinations were made with mixtures containing nitrogen tetroxide at ambient and at elevated temperatures in the apparatus illustrated in Figure 18. This apparatus consisted of a 2-inch glass explosion pipe A, 18 inches long, closed at the top by a ground glass plate and at the bottom by a teflon-covered stopper. Electrodes at the base supported an ignition coil of .005-inch diameter platinum wire C. Heater E was used to bring the nitrogen tetroxide to the desired test temperature. Mixing was accomplished mechanically by use of an external magnet and a teflon-coated soft iron core mixer B.

The desired composition of the test mixture was attained by the method of partial pressures. Tests were conducted by first evacuating tube A; fuel vapors were then added from reservoir E until the desired pressure (as noted on manometer F) was attained. Finally, sufficient nitrogen tetroxide was admitted to the system to bring the final pressure to one atmosphere (as noted on manometer G). After mixing for less than one minute, the platinum wire was fused. A mixture was considered flammable if a flame propagated the full length of the explosion tube.
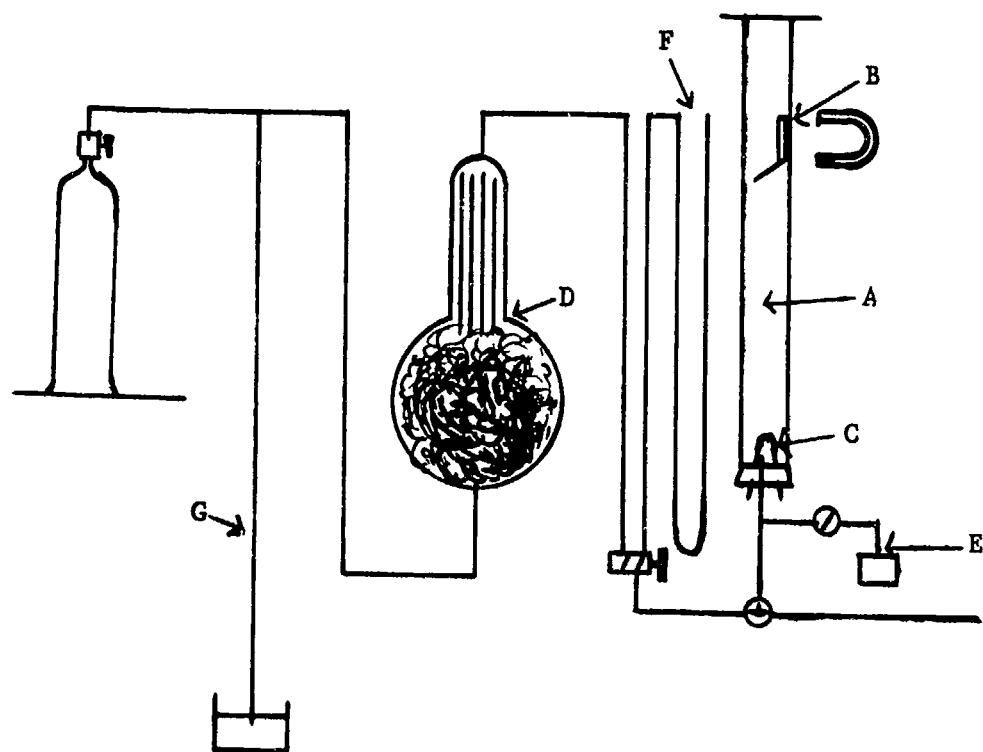
Figure 18. - Apparatus for determination of limits of flammability for mixtures containing nitrogen tetroxide.

APPENDIX V

Combustion of Heterogeneous Single-Phase Mixtures

The apparatus used to determine the flammability characteristics of layers of gaseous combustible and air is shown in Figure 19. The main body of the apparatus consists of a 10-inch spherical stainless steel chamber a, in the center of which is located a 2-inch cylinder b, 1.5-inch high. The homogeneous combustible gas mixture to be tested is placed in this cylinder and the ends of the cylinder b are then closed by spring-loaded sliding vane seals c and d. Two-inch cylinders e, 1.2-inch high and open at both ends, are attached to the sliding vane seals in such a manner that when the seals are opened, they slide into place over the ends of cylinder b. Oil-saturated felt pads are fastened to cylinders e to provide a seal between them and cylinder b. The desired gas mixture is prepared by use of flowmeter f, liquid fuel feed g and mixer h. The liquid fuel feed consists of a geared, motor-driven syringe which injects the liquid fuel into the heated tubing j where it rapidly vaporizes and mixes with the incoming air.

Ignition source k consists of a 1-inch coil of 0.005-inch-diameter platinum wire. In practice, it is fused by a 110-volt discharge from a 20 μf capacitor. The pressure developed during combustion is recorded with a piezoelectric pressure transducer l which is connected to an oscilloscope equipped with a Polaroid camera. A sequence switch (not shown) provides the necessary electrical impulses required to open the solenoid-actuated sliding vanes d and c, trigger the oscilloscope and fuse the ignition wire.

In conducting a test, the desired gas mixture is used to purge cylinder b for 10 minutes at a flow rate of one liter/min. The flow is then stopped and the sequence switch started. This switch first actuates the vane solenoids and then swings the cylinder*e into place over the chamber b. Following a preset time interval for diffusion of the gases, the oscilloscope sweep is triggered and the ignition source wire is fused. The Polaroid camera records the resultant oscilloscope trace and the system is readied for the next test.

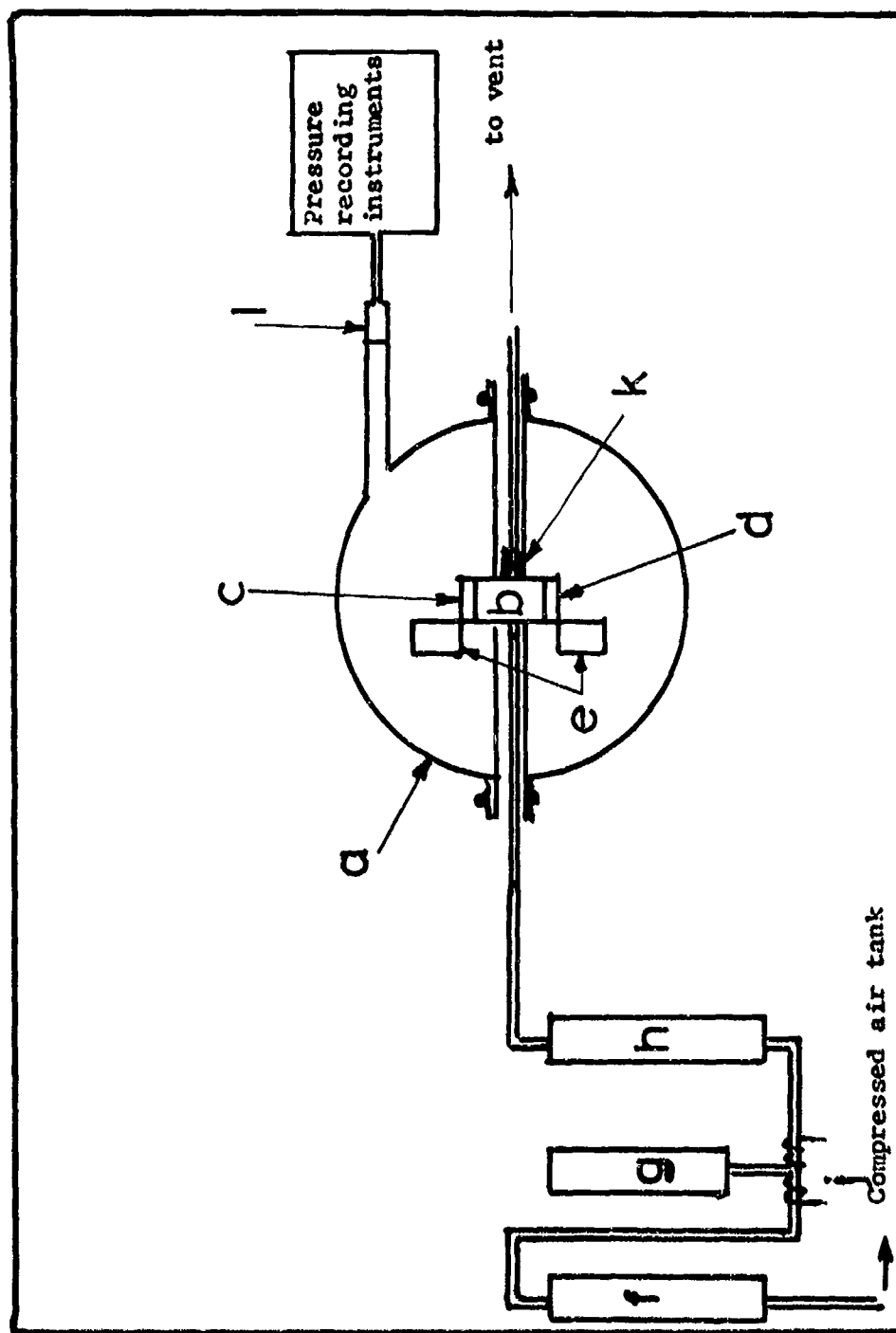* In the tests considered here only the upper vane C was opened.

Figure 19. Apparatus used in the study of flammability characteristics of stratified (or layered) combustible—air mixtures.

APPENDIX VI

Liquid Burning Rates

Figure 20 gives a diagram of the apparatus used to measure the liquid regression rates of liquid combustibles burning in nitrogen tetroxide-air atmospheres. The outer tank $\underline{a}$ and flue are first filled with the desired nitrogen tetroxide-air mixture. The liquid combustible is added to the tray $\underline{b}$ and the liquid level noted on indicator $\underline{c}$. A spark ignition source $\underline{d}$ is used to ignite the vapors near the liquid surface and the rate of regression of the burning surface is observed on indicator $\underline{c}$. The hot product gas is expelled through flue $\underline{e}$ and as the dense nitrogen tetroxide-air mixture is consumed, air enters through vents $\underline{f}$ to maintain a constant flow of oxidant over the liquid pool.
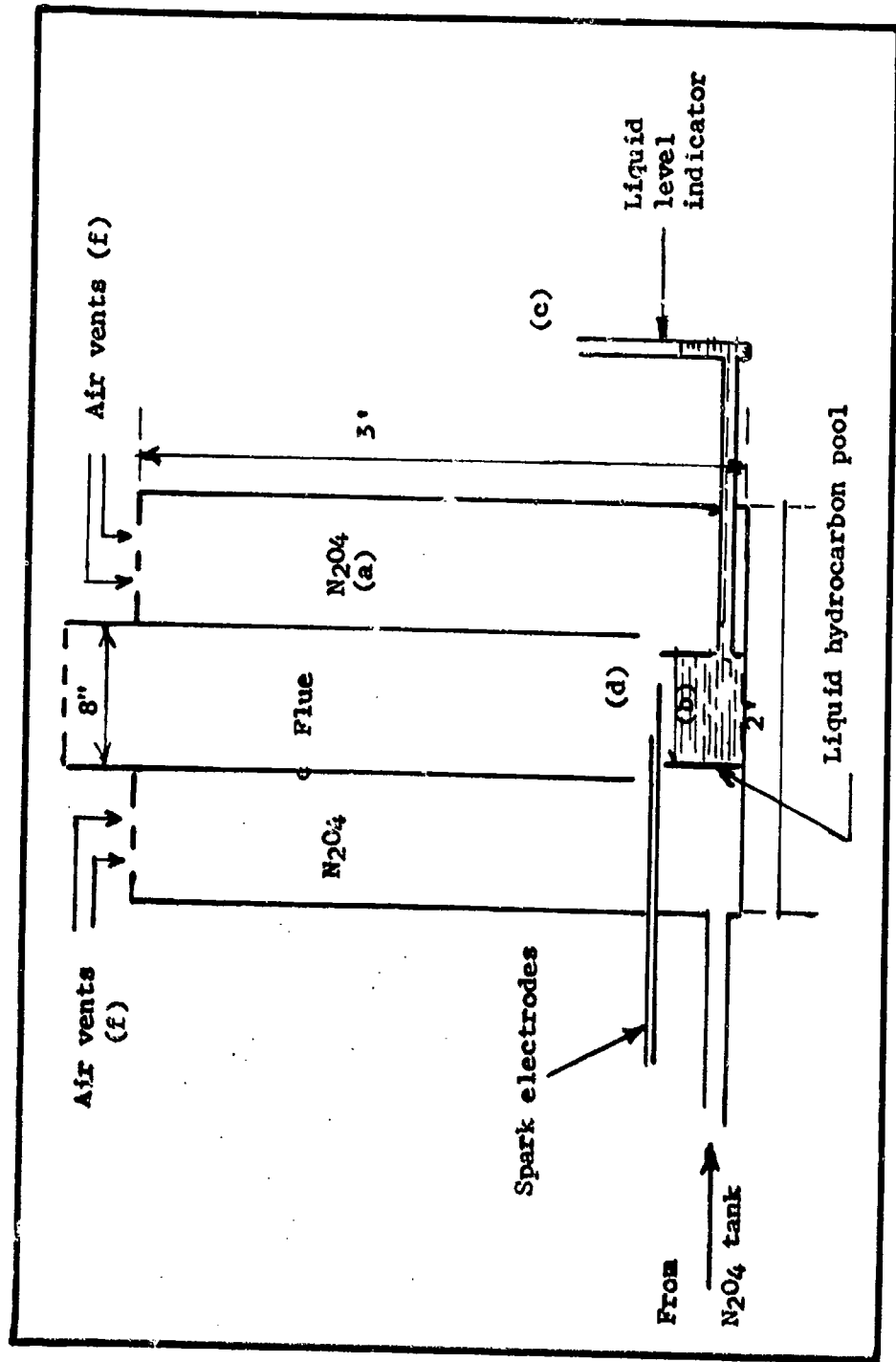
Figure 20. Apparatus used for measuring liquid regression rates of hydrocarbons and other fuels.

APPENDIX VII

Flame Arrester Studies

A general diagram of the apparatus used in evaluating various arresters in flowing streams is shown in Figure 21. It consists of a compressor, four air-storage tanks, a filter, a pentane or natural gas supply, a 2-inch glass tube, a spark source, the arrester* to be evaluated and a 12-inch discharge tee. A detailed drawing of the pentane supply, glass pipe and arrester is given in Figure 22. This figure shows the layout used in conducting flame penetration tests with pentane-air mixtures; a drum camera was used in place of the 35 mm. Fastax camera in some experiments.

The flame arrester apparatus was also used in conducting blowoff experiments. In these, air-flow was also established with a 900 cfm. blower through a 6-inch glass pipe placed around the 2-inch glass pipe; the pentane-air mixtures were ignited above the 2-inch pipe in this case.

To conduct a flame arrester test, the desired air flow was first established; air-flow rate measurements were made with a pitot tube inserted in the air supply line just above the pentane (or natural gas) inlet. Pentane (or natural gas) was then added to produce a flammable mixture in the downstream sections and in the arrester (wire gauze or tube bundle). The flammable mixture was ignited by electrical spark located 34 inches below the arrester, and the resultant flame was photographed with the Fastax (or drum) camera. The photographic records were used to determine the flame approach velocity (rate at which flame approached the arrester) and whether flame penetrated the arrester. In some experiments, flame was initiated above the arrester and permitted to propagate downward toward the arrester against the flow. In the blowoff experiments, ignition was attempted above the 2-inch glass pipe with various quantities of air flowing through the annular space between the 6-inch and 2-inch glass pipes.

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* The arresters were made of 20-mesh (Tyler) brass wire gauze, 200-mesh (U.S. Standard) brass wire gauze, 0.181-inch ID by 0.25-inch OD stainless steel or aluminum tubing 6 inches long and .0857-inch ID by 0.0937-inch OD stainless steel tubing 6 inches long; the 6-inch tubes were held in place by coarse screens.
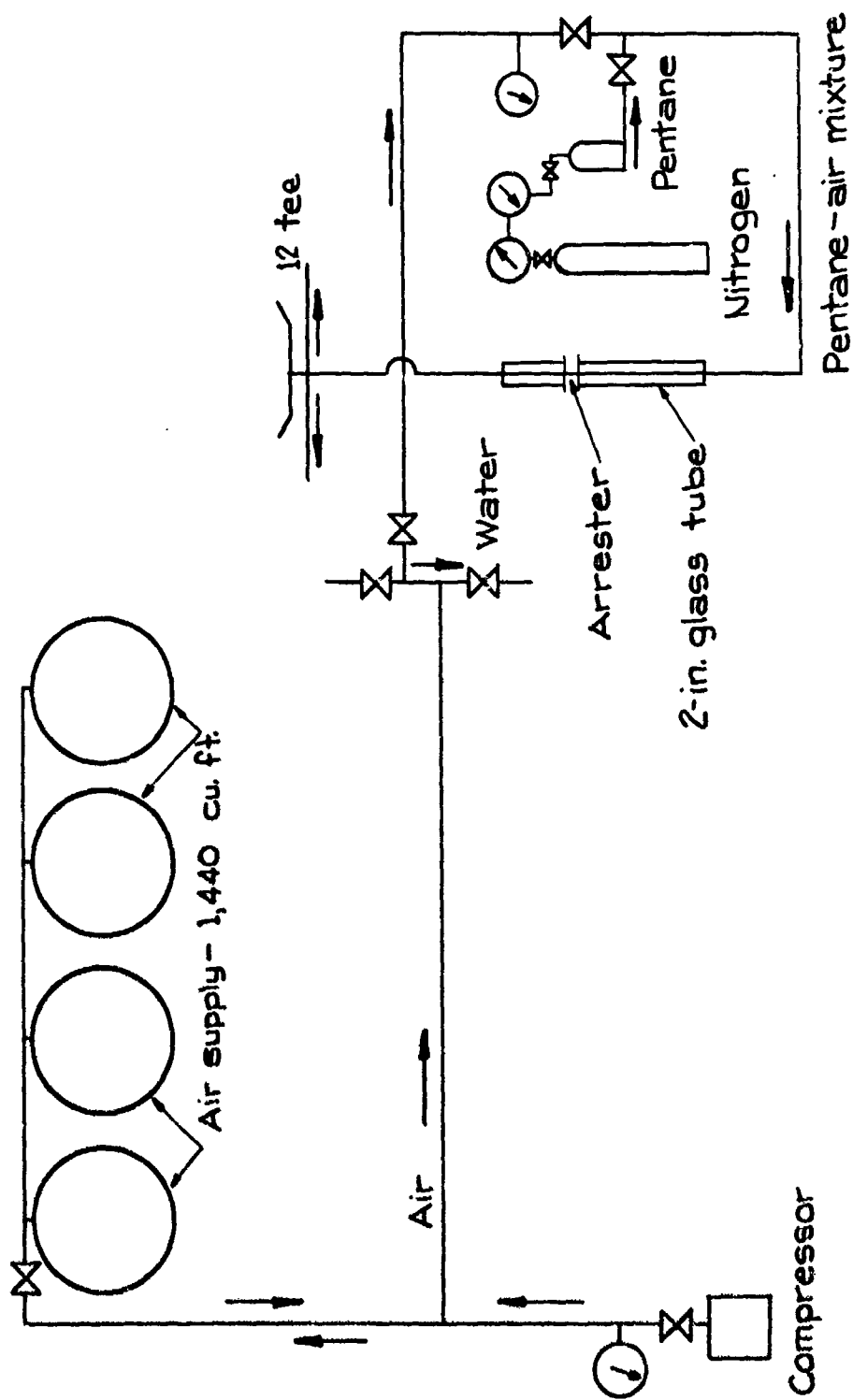
Figure 21. Schematic of air supply for high mixture flow rates.
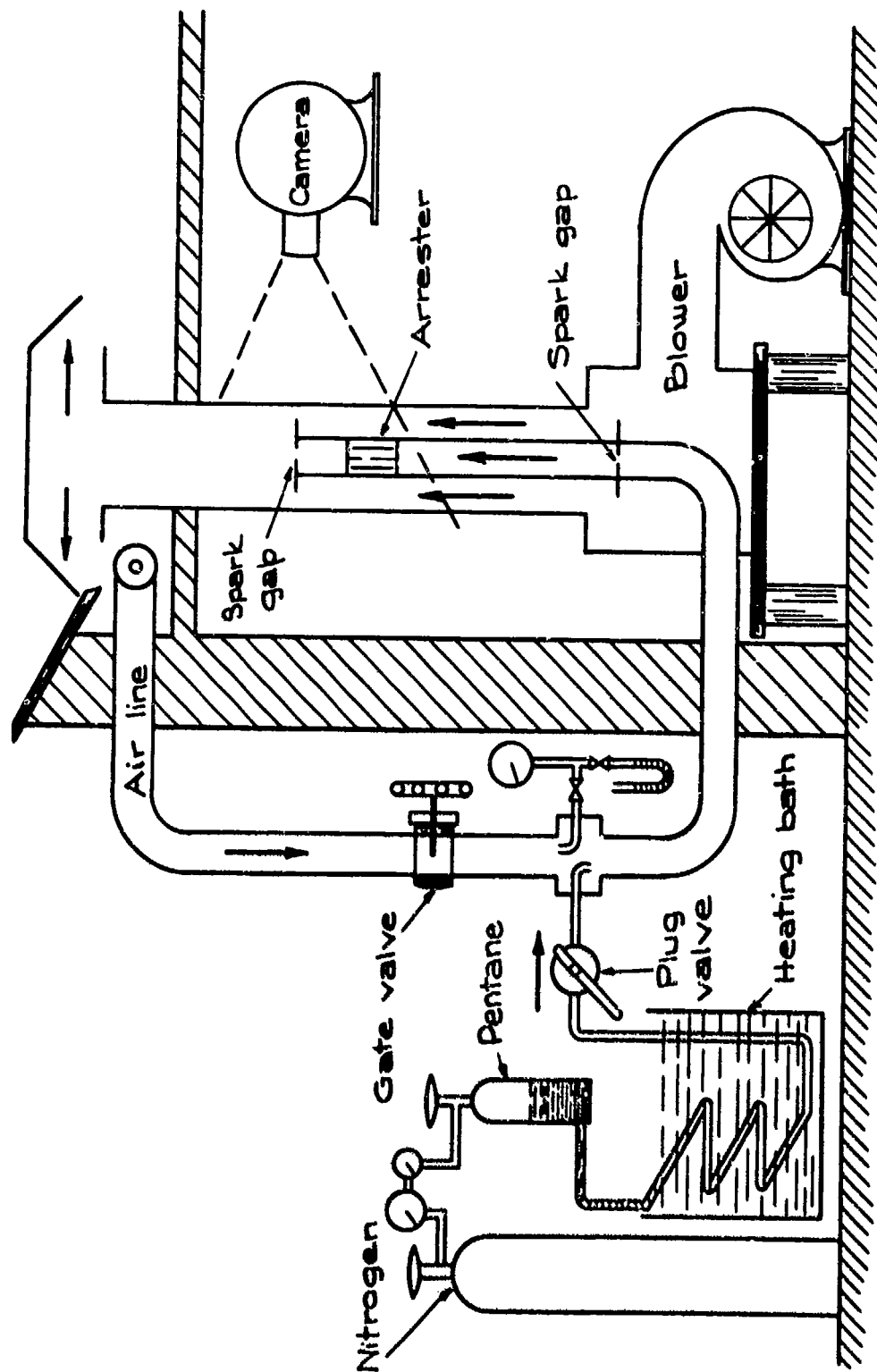
Figure 22. - Apparatus for evaluating flame arresters and flash-back in high velocity streams.

1. Combustion
2. Fires
3. Combustible-oxidant systems
I. AFSC Project 6075, Task 607504
II. Contract DO 33 (616)60-8
III. Bureau of Mines, U. S. Dept. of the Interior, Pittsburgh, Pa.
IV. G. S. Scott, et al.
V. Aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Aeromechance, Flight Accessories Lab, Wright-Patterson AFB, Ohio.
Rpt Nr ASD-TR-61-278, Suppl 1. REVIEW OF FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES. Final report, Oct 62, 43p-incl illus., tables, 11 refs.
Unclassified report

The prevention of fires and explosions involving the combustibles and oxidants likely to be found in flight vehicles requires a knowledge of the flammability and related characteristics of these materials. This report, the second in a series, presents the results of experimental studies of certain

(over)

phases of the general problem where information was lacking or insufficient. These include: Ignition energy requirements and limits of flammability of selected combustibles in oxidants other than air; effect of blending of fuels on the spontaneous ignition temperature; effect of temperature on the limits of flammability and minimum oxygen requirements for flame propagation of selected combustibles; behavior of layered vapor and liquid-vapor mixtures in various oxidizing atmospheres; behavior of flame arrestors in static and in laminar and turbulent flowing mixtures.

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